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Palladium–iminophosphine-catalyzed homocoupling of alkynylstannanes and other organostannanes using allyl acetate or air as an oxidant

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Abstract

A palladium–iminophosphine complex was found to catalyze the homocoupling reaction of alkynylstannanes using allyl acetate as an oxidant, whereas aryl- and alkenylstannanes were oxidatively homocoupled with air.
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1. Introduction

Ligands often play important roles in transition metal catalysis. We disclosed that a palladium complex coordinated by an iminophosphine ligand shows a marked preference for alkynylstannanes to alter the catalytic cycle of the palladium-catalyzed cross-coupling reaction [1,2]. Thus, in contrast to the generally accepted catalytic cycle for the palladium-catalyzed coupling of organostannanes including alkynylstannanes with aryl iodides, the one using an iminophosphine ligand starts with the oxidative addition of an alkynylstannane to a palladium(0) complex. The activation of carbon–tin bonds by a palladium–iminophosphine catalyst has been utilized for the addition of alkynylstannanes to alkynes [3]. Here we report that the affinity of the palladium–iminophosphine for alkynylstannanes enables the homocoupling of alkynylstannanes with a mild oxidant such as allyl acetate and that the oxidative homocoupling was applied also to aryl- and alkenylstannanes by use of air as an oxidant [4]. Although there have been many reports on the palladium-catalyzed homocoupling of organostannanes owing to high availability, stability and chemoselectivity of organostannanes, no method utilizes such a mild but unusual oxidant as allyl acetate [5].

During our investigation of the palladium–iminophosphine-catalyzed carbostannylation of alkynes, we found that the reaction of an alkynylstannane with allyl propiolate gave the homocoupling product of the alkynylstannane in addition to an addition product of the alkynylstannane to the triple bond of allyl propiolate. Therefore, we expected that allyl acetate, which lacks a carbon–carbon triple bond, should work effectively as an oxidant in the homocoupling of alkynylstannanes.

2. Results and discussion

The reaction of tributyl(phenylethynyl)tin (**1a**) with allyl acetate (one equivalent) in the presence of a catalytic amount of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (2.5 mol%) and *N*-(2-diphenylphosphinobenzylidene)aniline (**IP**, 5 mol%) in DMF for 4 h at 40 °C gave 1,4-diphenyl-1,3-butadiyne (**2a**) in 86% yield, whereas the cross-coupling product (**3a**) of **1a** with allyl acetate was not detected (Scheme 1 and entry 1 of Table 1). Use of triphenylphosphine (10 mol%) instead of **IP** drastically retarded the reaction (entry 2), whereas the reaction

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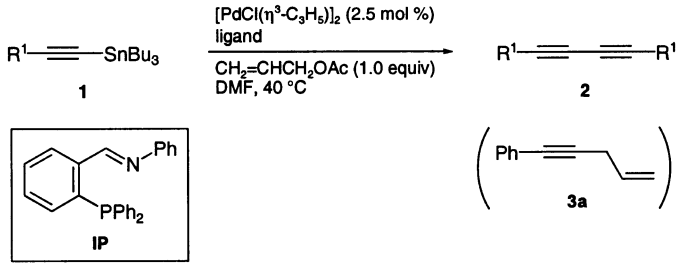


Scheme 1.

Table 1
Homocoupling of alkynylstannanes catalyzed by a palladium–iminophosphine complex using allyl acetate as an oxidant

Entry	Ligand (mol%)	R^1 in **1**	Time (h)	Conv. (%) [a]	Yield (%) of **2** [b]
1	**IP**(5)	Ph	4	>99	86
2	PPh_3(10)	Ph	4	14	13 [c]
3	None	Ph	4	60	11 [d]
4	**IP**(5)	4-CF_3–C_6H_4	1	>99	92
5	**IP**(5)	4-MeO–C_6H_4	1	>99	93
6	**IP**(5)	2-CF_3–C_6H_4	1	>99	90
7	**IP**(5)	Bu	1	>99	84

The reaction was carried out at 40 °C in DMF (2 ml) under an argon atmosphere using an alkynylstannane (0.32 mmol) and allyl acetate (0.32 mmol) in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (8.0 μmol) and **IP** (16 μmol).

[a] Determined by ^{1}H- and/or ^{119}Sn-NMR.

[b] Isolated yield based on alkynylstannane.

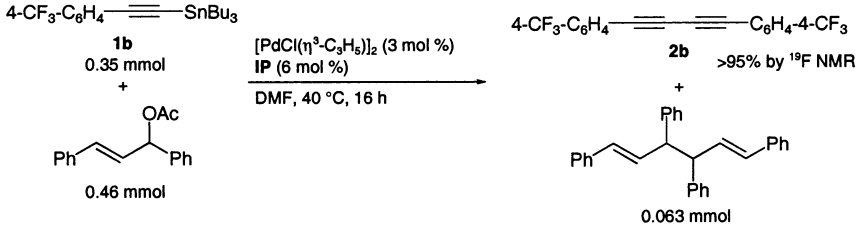
[c] Cross-coupling product **3a** was obtained in 1% yield.

[d] Cross-coupling product **3a** was obtained in 3% yield.

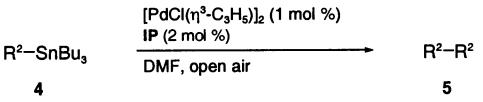
without any ligand gave only 11% yield of **2a**, which was accompanied by the formation of cross-coupling product **3a** (entry 3). The Pd–**IP** catalyst was applied to the homocoupling of various alkynylstannanes. Arylethynylstannanes generally gave the corresponding 1,3-diynes in good yields, irrespective of the kind of the substituent on the phenyl ring (entries 4–6). Tributyl(1-hexyn-1-yl)tin also reacted smoothly to give 5,7-dodecadiyne in a good yield (entry 7).

In order to pursue how the allyl moiety changes, we used 1,3-diphenylpropen-3-yl acetate in the homocoupling of tributyl[(*p*-trifluoromethylphenyl)ethynyl]tin (**1b**) as shown in Scheme 2. The allylic acetate actually acted as an oxidant and underwent reductive coupling to give 1,3,4,6-tetraphenyl-1,5-hexadiene as a mixture of diastereomers, though how they were produced is yet unclear at present. Again, the corresponding cross-coupling product was not detected. It is worthy of note that allylic acetates do not couple with alkynylstannanes in the presence of a palladium catalyst in spite that some reports on the cross-coupling of allylic electrophiles with organostannanes are recorded in the literature [6].

Unfortunately, the Pd–**IP**/allyl acetate system is not applicable to the homocoupling reaction of organostannanes other than alkynylstannanes mainly due to the competitive cross-coupling reaction. Aryl- and alkenylstannanes, however, underwent the homocoupling reaction with the Pd–**IP** catalyst in combination with air as oxidant (Scheme 3 and Table 2). For example, treatment of tributyl(phenyl)tin in an open air with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (1 mol%) and **IP** (2 mol%) in DMF for 4 h at 70 °C gave biphenyl in 66% yield (entry 1). Other aryl- and heteroarylstannanes with an electron-withdrawing or electron-donating substituent reacted smoothly in the presence of the Pd–**IP** catalyst in the open air to give the corresponding biaryls in moderate to good yields (entries 2–10). A styrylstannane underwent the homo-



Scheme 2.



Scheme 3.

Table 2
Homocoupling of organostannanes catalyzed by Pd–**IP** in an open air

Entry	R^2 in **4**	Temperature (°C)	Time (h)	Yield (%) of **5** [a]
1	Ph	70	4	66
2 [b]	4-CF_3–C_6H_4	40	4	87
3	4-O_2N–C_6H_4	50	5	84
4	4-OHC–C_6H_4	50	36	76
5	4-MeO–C_6H_4	70	102	81
6	2-NC–C_6H_4	50	44	80
7	4-$HOCH_2$–C_6H_4	70	10	75
8	3-MeOCOO–C_6H_4	50	2.5	60
9	2-thienyl	50	53	60
10	2-pyridyl	70	72	79
11 [c]	(*E*)-PhCH=CH	50	4	68
12	PhC≡C	50	6	31
13	BuC≡C	50	11	34

The reaction was carried out in DMF (2 ml) in an open air using an organostannane (0.80 mmol) in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (8.0 μmol) and **IP** (16 μmol).

[a] Isolated yield based on organostannane.

[b] With 5 mol% of Pd–**IP**.

[c] (*E*,*E*)-1,4-Diphenyl-1,3-butadiene was obtained.

coupling, retaining their configuration (entry 11). On the other hand, the yields of homocoupling products of alkynylstannanes were much lower than those using allyl acetate (entries 12 and 13).

3. Conclusion

We have demonstrated that the palladium–iminophosphine complex is an effective catalyst for the oxidative homocoupling of organostannanes, where allyl acetate and air complementarily work as an oxidant: the former is effective for alkynylstannanes and the latter for aryl- and alkenylstannanes.

4. Experimental

4.1. General remarks

All manipulations of oxygen- and moisture-sensitive materials were conducted with the standard Schlenk techniques under a purified argon atmosphere (deoxygenated by passing through BASF-Catalyst R3-11 column at 80 °C). Silica gel column chromatography was performed using Wakogel C-200. Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^{1}H, 270 MHz; ^{31}P, 109 MHz; ^{119}Sn, 101 MHz) or Varian Mercury 200 (^{1}H, 200 MHz; ^{13}C, 50.3 MHz; ^{19}F, 188 MHz) spectrometer using tetramethylsilane (^{1}H) as an internal standard, and 20% trifluoroacetic acid (^{19}F), 85% phosphoric acid (^{31}P), and tetramethyltin (^{119}Sn) as external standards. High-resolution mass spectra were obtained with a JEOL JMS-HX110A spectrometer. The preparative recycling gel permeation chromatography was performed with a JAI LC-908 equipped with JAIGEL-1H and -2H columns (chloroform as an eluent). All melting points were measured with a Yanagimoto–Seisakusho Micro Melting Point apparatus without corrected. Elemental analyses were performed at the Microanalytical Center, Kyoto University. Following compounds were prepared according to the corresponding literature procedure: (*E*)-tributyl(2-phenylethenyl)tin [7], tributyl(phenylethynyl)tin [8], tributyl(1-hexyn-1-yl)tin [9], tributyl[4-(trifluoromethyl)phenyl]tin [10], tributyl(4-nitrophenyl)tin [11], tributyl(4-formylphenyl)tin [12], tributyl(4-methoxyphenyl)tin [13], tributyl[4-(hydroxymethyl)phenyl]tin [14], 2-(tributylstannyl)thiophene [15]. Other alkynylstannanes were prepared according to the literature procedure [16].

4.2. Preparation of *N*-(2-diphenylphosphinobenzylidene)aniline (*IP*) [17]

A mixture of 2-diphenylphosphinobenzaldehyde [18] (0.50 g, 1.72 mmol) and aniline (166 mg, 1.78 mmol) in toluene (15 ml) was stirred at a reflux temperature for 19 h. The mixture was concentrated under a reduced pressure, and the residue was treated with hexane (20 ml). Filtration of insoluble material gave **IP** (0.62 g, 99% yield) as a light yellow solid: m.p. 109–112 °C; ^{1}H-NMR ($CDCl_3$) δ 6.86–6.98 (m, 3H), 7.10–7.50 (m, 15H), 8.16–8.25 (m, 1H), 9.07 (d, $J = 5.2$ Hz, 1H); ^{31}P{^{1}H}-NMR ($CDCl_3$) δ −12.7; Anal. Calc. for $C_{25}H_{20}NP$: C, 82.17; H, 5.52; N, 3.83. Found: C, 82.07; H, 5.69; N, 3.58.

4.3. Preparation of tributyl(2-cyanophenyl)tin

A 1.67 M hexane solution of BuLi (20 ml, 33 mmol) was added dropwise to a solution of 2-bromobenzonitrile (6.6 g, 36 mmol) in THF (30 ml) at −78 °C, and the mixture was stirred at −78 °C for 1 h. To the mixture was added tributyltin chloride (9.1 g, 28 mmol) at −78 °C and the temperature was allowed to rise gradually up to room temperature. After 12 h, the mixture was poured into water (50 ml) and extracted with diethyl ether (150 ml × 2). The combined organic layer was washed successively with water (50 ml) and brine (50 ml), and dried over anhydrous magnesium sulfate. Evaporation of the solvent was followed by

silica gel column chromatography (hexane/ethyl acetate = 98/2) to give tributyl(2-cyanophenyl)tin (3.0 g, 27% yield) as a colorless oil: ^{1}H-NMR ($CDCl_3$) δ 0.82–1.78 (m, 27H), 7.31–7.42 (m, 1H), 7.43–7.58 (m, 2H), 7.59–7.71 (m, 1H). Anal. Calc. for $C_{19}H_{31}NSn$: C, 58.19; H, 7.97; N, 3.57. Found: C, 58.00; H, 8.02; N, 3.43.

4.4. Preparation of tributyl(3-methoxycarbonyloxyphenyl)tin

To a 1.0 M THF solution of Bu_4NF (6.5 ml, 6.5 mmol) was added tributyl[3-*tert*-butyl(dimethyl)silyloxyphenyl]tin [19] (1.63 g, 3.28 mmol), and the mixture was stirred at room temperature. After 1 h, the mixture was poured into a saturated NH_4Cl aqueous solution (16 ml) and extracted with ethyl acetate (50 ml × 2). The combined organic layer was washed successively with water (30 ml) and brine (30 ml), and dried over anhydrous magnesium sulfate. Evaporation of the solvent was followed by silica gel column chromatography (hexane/ethyl acetate = 20/1) to give tributyl(3-hydroxyphenyl)tin (0.78 g, 62% yield) as a colorless oil: ^{1}H-NMR ($CDCl_3$) δ 0.82–1.72 (m, 27H), 5.62 (s, 1H), 6.73–6.80 (m, 1H), 6.90–7.28 (m, 3H). Anal. Calc. for $C_{18}H_{32}OSn$: C, 56.42; H, 8.42. Found: C, 56.19; H, 8.45.

A solution of tributyl(3-hydroxyphenyl)tin (3.5 g, 0.92 mmol) in THF (2 ml) was added to a suspension of NaH (60% dispersion in mineral oil, 40 mg, 1.0 mmol) in THF (2 ml) at 0 °C, and the mixture was stirred for 0.5 h at room temperature. To this solution was added methyl chloroformate (95 mg. 1.0 mmol), and the resulting mixture was stirred overnight. The mixture was poured into a saturated NH_4Cl aqueous solution (3 ml), and extracted with ethyl acetate (10 ml × 2). The combined organic layer was washed with water (5 ml) and brine (5 ml), and dried over anhydrous magnesium sulfate. Evaporation of the solvent was followed by silica gel column chromatography (hexane/ethyl acetate = 10/1) to give tributyl(3-methoxycarbonyloxyphenyl)tin (0.34 g, 84% yield) as a colorless oil: ^{1}H-NMR ($CDCl_3$) δ 0.81–1.75 (m, 27H), 3.91 (s, 3H), 7.04–7.18 (m, 1H), 7.18–7.45 (m, 3H). Anal. Calc. for $C_{20}H_{34}O_3Sn$: C, 54.45; H, 7.77. Found: C, 54.68; H, 8.05.

4.5. General procedure for the Pd–**IP**-catalyzed homocoupling of alkynylstannanes using allyl acetate

An alkynylstannane (0.32 mmol) was added to a solution of allyl acetate (0.32 mmol), **IP** (6.0 mg, 16 μmol) and $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (3.0 mg, 8.0 μmol) in DMF (2 ml), and the resulting mixture was stirred at 40 °C for the time depicted in Table 1. Quenching with water (10 ml), extraction with diethyl ether (30 ml), washing the combined organic layer with water (10 ml × 3) and brine (10 ml), drying the organic layer over anhydrous magnesium sulfate, and evaporation, followed by gel permeation chromatography, gave the corresponding coupling product. The results are summarized in Table 1.

All of the products listed in Table 1 have already been reported in the literature. Their spectroscopic data are as follows.

1,4-Diphenyl-1,3-butadiyne [20]: ^{1}H-NMR ($CDCl_3$) δ 7.30–7.40 (m, 6H), 7.49–7.58 (m, 4H).
1,4-Bis(4-trifluoromethylphenyl)-1,3-butadiyne [21]: ^{1}H-NMR ($CDCl_3$) δ 7.50–7.80 (m).
1,4-Bis(4-methoxyphenyl)-1,3-butadiyne [22]: ^{1}H-NMR ($CDCl_3$) δ 3.82 (m, 6H), 6.80–6.93 (m, 4H), 7.41–7.53 (m, 4H).
1,4-Bis(2-trifluoromethylphenyl)-1,3-butadiyne [23]: ^{1}H-NMR ($CDCl_3$) δ 7.40–7.90 (m).
5,7-Dodecadiyne [21]: ^{1}H-NMR ($CDCl_3$) δ 1.17 (t, J = 7.0 Hz, 6H), 1.20–1.85 (m, 8H), 2.52 (t, J = 6.3 Hz, 4H).

4.6. General procedure for the Pd–**IP**-catalyzed homocoupling of organostannanes using air

An organostannane (0.80 mmol) was added to a solution of **IP** (6.0 mg, 16 μmol) and $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (3.0 mg, 8.0 μmol) in DMF (2 ml), and the resulting mixture was stirred at the temperature for the time both indicated in Table 2. Quenching with water (10 ml), extraction with ethyl acetate (30 ml × 2), washing the combined organic layer with water (10 ml) and brine (10 ml), drying the organic layer over anhydrous magnesium sulfate, and evaporation, followed by gel permeation chromatography, gave the corresponding coupling product. The yields are listed in Table 2.

3,3′-Bis(methoxycarbonyloxy)biphenyl: A pale yellow oil, ^{1}H-NMR ($CDCl_3$) δ 3.92 (s, 6H), 7.13–7.24 (m, 2H), 7.36–7.53 (m, 6H); ^{13}C-NMR ($CDCl_3$) δ 55.4, 119.8, 120.3, 124.8, 129.9, 141.7, 151.5, 154.2; HRMS (FAB+) Calc. for $C_{16}H_{15}O_6$: $M^+ + H$, 303.0868. Found: *m/z* 303.0865.

Other products listed in Table 2 have already been reported in the literature. Their spectroscopic data are as follows.

Biphenyl: ^{1}H-NMR ($CDCl_3$) δ 7.29–7.51 (m, 6H), 7.55–7.65 (m, 4H).
4,4′-Dinitrobiphenyl: m.p. 238–240 °C ([24], 241–244 °C); ^{1}H-NMR ($CDCl_3$) δ 7.72–7.83 (m, 4H), 8.30–8.42 (m, 4H).
4,4′-Diformylbiphenyl: m.p. 144–146 °C ([25], 145 °C); ^{1}H-NMR ($CDCl_3$) δ 7.78–7.84 (m, 4H), 7.98–8.03 (m, 4H), 10.10 (s, 2H).

4,4′-Dimethoxybiphenyl [26]: ^{1}H-NMR ($CDCl_3$) δ 3.84 (s, 6H), 6.91–7.02 (m, 4H), 7.42–7.54 (m, 4H).
2,2′-Dicyanobiphenyl [27]: ^{1}H-NMR ($CDCl_3$) δ 7.53–7.62 (m, 4H), 7.69–7.77 (m, 2H), 7.81–7.87 (m, 2H).
4,4′-Bis(hydroxymethyl)biphenyl: m.p. 193–194 °C ([28], 188–189 °C); ^{1}H-NMR ($CDCl_3$) δ 4.75 (brs, 4H), 7.41–7.51 (m, 4H), 7.56–7.65 (m, 4H).
2,2′-Bithiophene [29]: ^{1}H-NMR ($CDCl_3$) δ 6.96–7.06 (m, 2H), 7.14–7.28 (m, 4H).
2,2′-Bipyridine: ^{1}H-NMR ($CDCl_3$) δ 7.27–7.37 (m, 2H), 7.77–7.89 (m, 2H), 8.36–8.45 (m, 2H), 8.66–8.74 (m, 2H).
(E,E)-1,4-Diphenylbutadiene: ^{1}H-NMR ($CDCl_3$) δ 6.52–6.75 (m, 2H), 6.80–7.05 (m, 2H), 7.15–7.52 (m, 10H).

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