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Review

The palladium–iminophosphine catalyst for the reactions of organostannanes☆

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Abstract

A palladium complex coordinated by an iminophosphine ligand was found to be a remarkably active catalyst for the coupling of organostannanes with aryl halides. The mechanistic studies show that the reaction of an alkynylstannane proceeds through an unprecedented catalytic cycle which involves an oxidative addition of the organostannane to the Pd(0)–iminophosphine complex. The catalyst was demonstrated to be also useful for the carbostannylation of alkynes and the homocoupling reaction of organostannanes. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cross-coupling; Carbostannylation; Homocoupling; Catalytic cycle; Oxidative addition

1. Introduction

The palladium-catalyzed cross-coupling of organostannanes with aryl halides is one of the most versatile carbon–carbon bond forming reactions featured by high chemoselectivity [1–3]. This means, however, that sometimes the reaction is not reactive enough and requires rather drastic conditions. The inertness of a C–Sn bond is evidenced also by the fact that the transition metal-catalyzed reaction of organostannanes other than the cross-coupling is extremely rare.

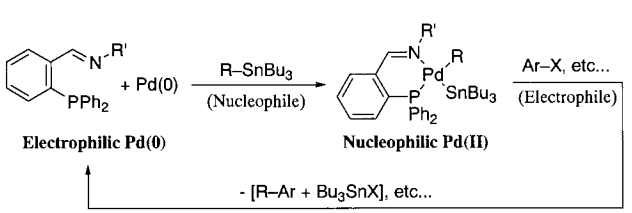
In this paper, we demonstrate that the cross-coupling reaction of organostannanes with aryl halides is efficiently catalyzed by a palladium complex coordinated by a bidentate iminophosphine ligand [4a]. We also discuss its catalytic cycles [4b], the carbostannylation of alkynes [4c] and the homocoupling reaction [4d,e].

The unique characters of the palladium complex coordinated by an iminophosphine may be attributed to a latent electrophilicity of the Pd(0) complex: the reaction with an organostannane nucleophile gives rise to a novel nucleophilic Pd(II) complex. This character contrasts sharply to that of a palladium complex with a conventional phosphine ligand and will be presented in the following chapters (Scheme 1).

2. Cross-coupling reaction of organostannanes with aryl halides

2.1. Introduction

The currently accepted catalytic cycle of the cross-coupling reaction of organostannanes with aryl halides



Scheme 1.

☆ Dedicated to Professor Jiro Tsuji and Richard F. Heck.

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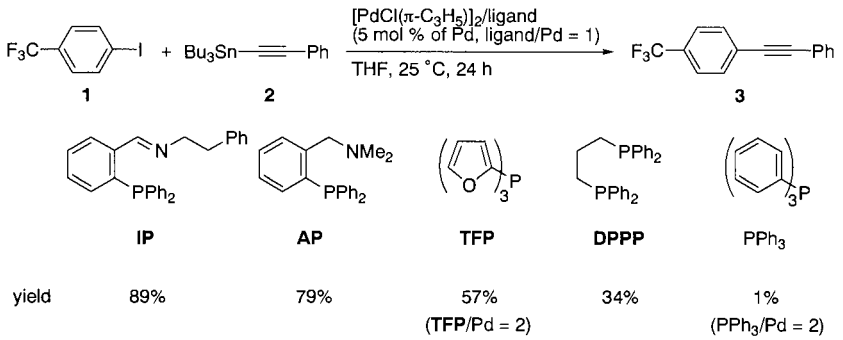


Scheme 2.

involves three distinct steps: (1) oxidative addition of an aryl halide to an electron-rich Pd(0) complex, (2) transmetalation of the resulting electrophilic Pd(II) complex with a nucleophilic organostannane, and (3) reductive elimination to give a cross-coupled product and regenerate the Pd(0) complex [5].

Farina and his co-workers surveyed the ligand for this coupling reaction and revealed that the reaction was accelerated in the magnitude of three orders by such a modest donor ligand as tri(2-furyl)phosphine or triphenylarsine as compared with triphenylphosphine [5]. The ligand is assumed to dissociate from a Pd(II) intermediate to make a vacant coordination site needed for the rate-determining transmetalation. This working hypothesis is rationalized by an inhibitory effect of an additional ligand and by the slow rates observed with a stronger donor like triphenylphosphine.

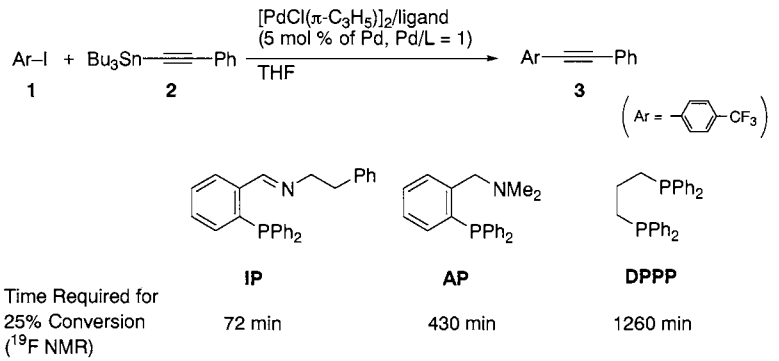
2.2. Palladium–iminophosphine as an active catalyst

Assuming that the reaction would proceed according to the catalytic cycle mentioned above, we expected that a palladium complex coordinated by an iminophosphine should be a good catalyst for the cross-coupling reaction for the following reason. An imino ligand is said to have a π-acceptor character [6] which would make a Pd(II) complex electrophilic to accelerate the reaction of Pd(II) with a nucleophilic organometallic reagent. In contrast, a phosphino group, which generally has a strong affinity to Pd(0), will assist the metal to react with an electrophile. Thus, the two different coordinating groups may play respective roles cooperatively in a catalytic cycle.

First, the catalytic activities of a palladium complex coordinated by *N*-(2-diphenylphosphinobenzylidene)-2-phenylethylamine (IP) and some other phosphine-based ligands were compared in the coupling reaction of 4-(trifluoromethyl)iodobenzene (**1**) with tributyl-(phenylethynyl)tin (**2**) (Scheme 2). IP was found to give higher reaction rate than any other palladium–phosphine complexes to give in 24 h 1-phenyl-2-(4-trifluoromethyl)phenylethyne (**3**) in 89% yield. A palladium complex coordinated by aminophosphine AP, where the imino moiety in IP is replaced by a dimethylaminomethyl group, was slightly less active, giving 79% of **3**. Under the same conditions, a palladium complex with tri(2-furyl)phosphine (TFP) complex (TFP/Pd = 2) or 1,3-bis(diphenylphosphino)propane (DPPP) gave **3** in 57 or 34% yield, respectively. The use of triphenylphosphine, one of the most conventional phosphine ligands, was not effective, giving only 1% yield of **3** [7].

It is noteworthy that P–N ligands IP and AP are more effective than TFP, which has been reported by Farina and his co-workers to be the best phosphine ligand for the palladium-catalyzed coupling of iodobenzene with tributyl(vinyl)tin [5]. They showed by kinetic study that the dissociation of a ligand from the Pd(II) intermediate to make a vacant coordination site for a vinyltin should be responsible for the high catalytic activity. In the reaction with IP, the expected intermediate in the catalytic cycle is complex **4** (cf. Scheme 4, vide infra) where both phosphino and imino groups coordinate to palladium through a six-membered chelate. Thus, the dissociation of either phosphorus or nitrogen atom in **4** is unlikely [8,9]. The fact that IP is more effective than TFP suggests that a vacant coordination site proposed by Farina is not always required for the present coupling reaction, or alternatively that the reaction proceeds through a different pathway by use of IP ligand. Contrary to the high yields observed with P–N ligands **IP**, **AP** and **DPPP** gave **3** in low yield. Thus, the coordination of the nitrogen atom appears to be essential for the high catalytic activity and formation of a six-membered chelate appears to be rather trivial.

In order to clarify the role of the nitrogen ligand, we compared the total rate of the cross-coupling reaction under the catalytic conditions and the rate of transmetalation step in a stoichiometric reaction using



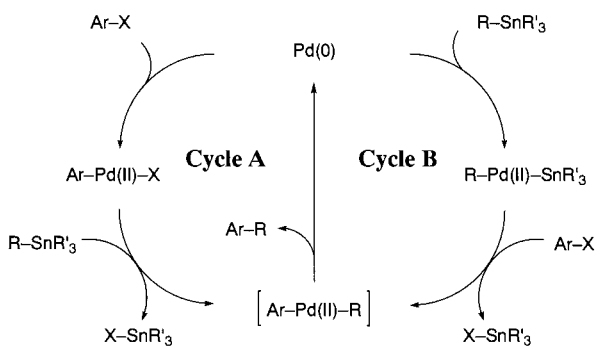
Scheme 3.

one of bidentate ligands IP, AP and DPPP (Schemes 3 and 4). The rate of the cross-coupling reaction in an early stage was estimated by the time ($T_{1/4}$) required for 25% conversion; the rate of transmetalation was estimated by the conversion of the reaction of Pd(II) complex **4**, **5** or **6** with **2** in 15 h. Although IP gave the highest rate for both reactions, AP gave a rate faster for the cross-coupling and slower for the transmetalation than DPPP. These results contrast sharply to the generally accepted catalytic cycle, where the rate of the cross-coupling reaction is proportional to the rate of the rate-determining transmetalation step. This discrepancy led us to propose a different catalytic cycle.

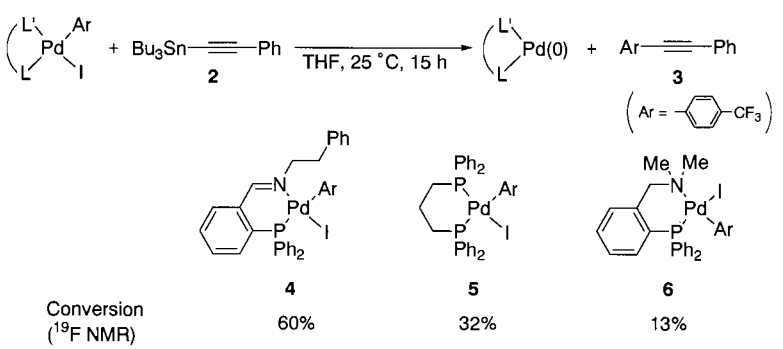
2.3. Alternative catalytic cycle

The currently accepted catalytic cycle for the coupling reaction is represented by Cycle A in Scheme 5, which starts with oxidative addition of an aryl halide to a Pd(0) complex. An alternative cycle must involve the reaction of a Pd(0) complex with an organostannane, the resulting Pd(II) complex then reacting with an aryl halide as illustrated by Cycle B in Scheme 5. However, this sort of catalytic cycle [10], or an oxidative addition of an organostannane to a Pd(0) complex [11], has never been presented before.

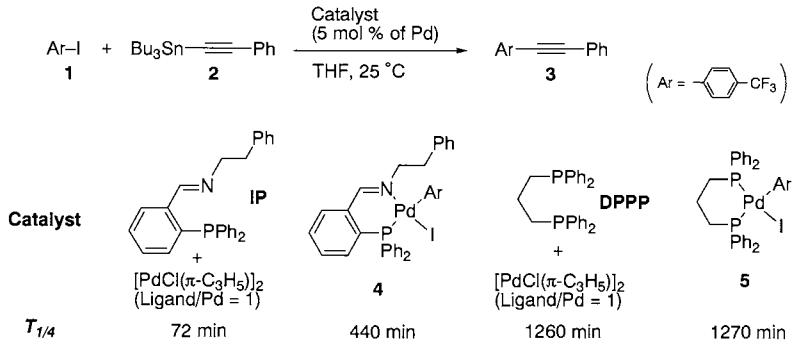
To gain an insight into the new catalytic cycle, we first examined the reaction rate of the palladium-catalyzed coupling of **2** with **1**, using IP or DPPP as a ligand (Scheme 6). According to Cycle A, complex **4** and **5**, prepared by the reaction of **1** with the corresponding Pd(0) complexes, are the expected intermediates. Thus, if the reaction would take place according to Cycle A, no induction period should be observed with either **4** or **5**, and the rates in the early stage of the reaction should be similar to or higher than those with the corresponding catalysts prepared in situ. If this is not the case, another catalytic cycle, Cycle B, must be working. To estimate the rate in the early stage of the reaction, we measured the time ($T_{1/4}$) required for 25% conversion. Conversion was monitored on the basis of consumed **1** by ^{19}F-NMR of the reaction mixture. When complex **4** or **5** was used as a catalyst, the



Scheme 5.



Scheme 4.



Scheme 6.

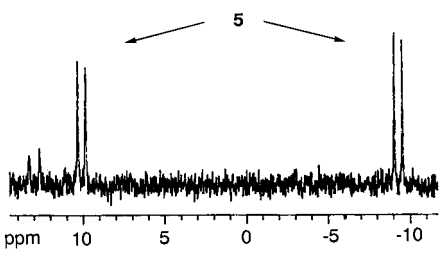


Fig. 1. $^{31}P\{^1H\}$-NMR (109 MHz) spectrum of the reaction mixture (at ca. 38% conversion) of the coupling of **2** with **1** in THF in the presence of [PdCl(π-C_3H_5)]–DPPP.

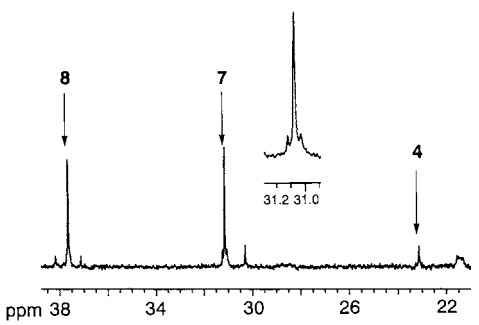
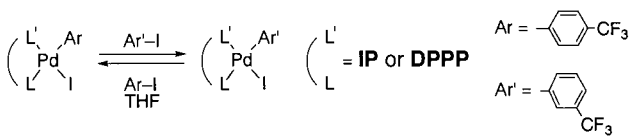


Fig. 2. $^{31}P\{^1H\}$-NMR (109 MHz) spectrum of the reaction mixture (at 2–33% conversion) of [PdCl(π-C_3H_5)]$_2$–IP catalyzed coupling of **2** with **1** in THF.



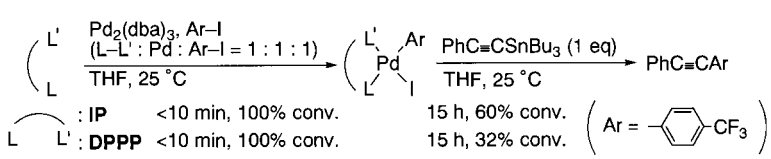
Scheme 7.

product directly derived from the complex also was counted in conversion.

We found that $T_{1/4}$ with preformed catalyst **4** was 440 min, much larger than $T_{1/4}$ (= 72 min) obtained with the catalyst prepared in situ from IP and [PdCl(π-C_3H_5)]$_2$. This means that the catalyst of [PdCl(π-C_3H_5)]$_2$–IP did not mediate the coupling reaction according to Cycle A. In contrast, the catalysts both preformed and in situ prepared with DPPP, promoted the reaction comparably, $T_{1/4}$ being 1270 and 1260 min, respectively. These results suggest that Cycle A is involved in these cases.

We next monitored by $^{31}P\{^1H\}$-NMR the behavior of the palladium complex during the reaction (Figs. 1 and 2). Since intermolecular exchange of an Ar group as shown Scheme 7 was not observed at 25°C in 1 d, oxidative addition of **1** to a palladium(0) complex coordinated by **IP** or **DPPP** must be irreversible. Thus, complex **4** or **5** [12], once produced, cannot but get into Cycle A. Furthermore, examinations under the stoichiometric conditions shown in Scheme 8 revealed that transmetalation was the rate-determining step in Cycle A.

The peaks assigned to complex **5** predominated in the reaction catalyzed by [PdCl(π-C_3H_5)]$_2$–DPPP (Fig. 1), showing that the reaction proceeded according to Cycle A and that transmetalation was the rate-determining step. By contrast, the reaction with [PdCl(π-C_3H_5)]$_2$–IP showed only a small amount of complex **4** (Fig. 2). If the reaction proceeded according to Cycle A, complex **4** must have been observed dominantly as discussed above, because the rate-determining step should be transmetalation. Instead, two major species were observed and identified as **7** and **8** (Figs. 2 and 3, [13,14]).



Scheme 8.

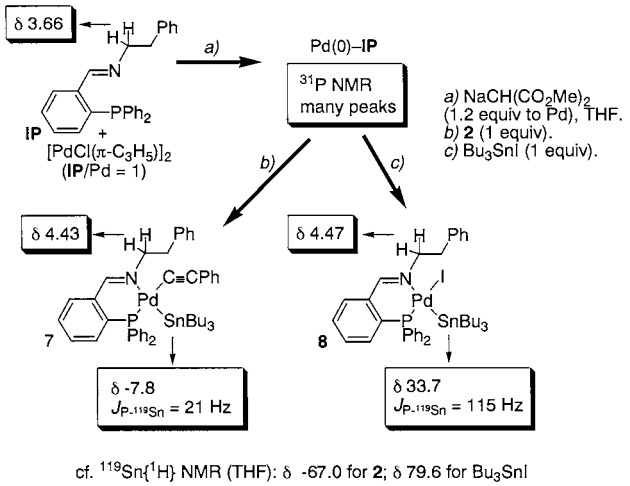


Fig. 3. $^{31}P\{^1H\}$-, $^{119}Sn\{^1H\}$- and ^1H-NMR (THF-d_8) parameters (chemical shift and J_{Sn-P}) of Pd(0)/IP and its reaction products with **2** or Bu_3SnI.

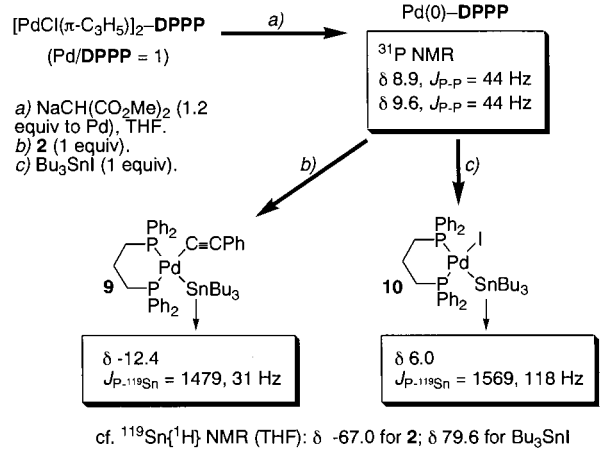
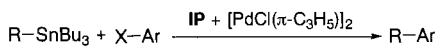


Fig. 4. $^{31}P\{^1H\}$-, $^{119}Sn\{^1H\}$- and ^1H-NMR (THF) parameters (chemical shift, J_{Sn-P} and J_{P-P}) of Pd(0)/DPPP and its reaction products with **2** or Bu_3SnI.

These were characterized in a following way: (1) formation of a Pd–Sn bond was confirmed by a large shift in ^{119}Sn-NMR, (2) coordination of the nitrogen was evidenced by a downfield shift (ca. 0.8 ppm) of the methylene protons adjacent to the nitrogen atom, and (3) the *cis*-configuration of the phosphino and stannyl groups was assigned on the basis of small coupling constants between phosphorous and tin ([11]a,b,d). Although the stoichiometric reaction of Pd(0)–DPPP with **2** or tributyltin iodide also generated the corresponding species **9** and **10** (Fig. 4), they were not detected under the conditions of the cross-coupling reaction (Fig. 1).

All these observations suggest that the coupling reaction of **2** with **1** using $[PdCl(\pi\text{-}C_3H_5)]_2$–IP as a catalyst should proceed through an oxidative addition of a C–Sn bond of an organostannane to a Pd(0) complex.



Scheme 9.

Namely, Cycle B in Scheme 5 accounts for all of the above observations.

2.4. Application to various organostannanes and aryl halides

High catalytic activity of the palladium complex coordinated by IP was also demonstrated in the cross-coupling of a variety of aryl halides with organostannanes (Scheme 9 and Table 1). The reaction of aryl iodides with **2** in the presence of 5 mol% of the catalyst gave over 86% yields of the corresponding ethynylation products, irrespective of an electron-withdrawing or -donating substituent on the phenyl group.

Table 1
Coupling of organostannanes with aryl halides catalyzed by a Pd–IP complex[a]

R–$SnBu_3$	Ar–X	Solvent	Temp (°C)	Time (h)	Yield (%) of R–Ar[b]
2	C_6H_5–I	THF	50	24	93
2	4-EtOCO–C_6H_4–I	THF	50	18	86
2	4-MeO–C_6H_4–I	THF	50	29	91
2	2-CF_3–C_6H_4–I	Toluene	80	32	92
2	4-Ac–C_6H_4–Br	Toluene	90	72	90
2	4-OHC–C_6H_4–Br	Toluene	90	48	84
2	C_6H_5–OTf[c]	Toluene	80	48	93
Tributyl(vinyl)tin[d]	4-EtOCO–C_6H_4–I	Toluene	90	43	90
Tributyl(phenyl)tin[e]	4-EtOCO–C_6H_4–I	Toluene	90	140	84

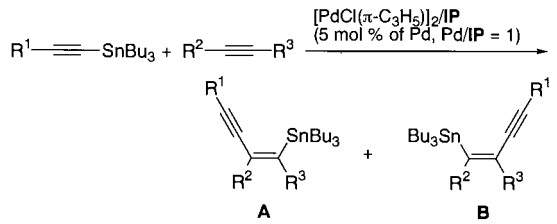
[a] The reaction was carried out in a solvent (5 ml) using an aryl halide (0.44 mmol), an organostannane (0.48 mmol), $[PdCl(\pi\text{-}C_3H_5)]_2$ (0.011 mmol) and IP (0.022 mmol).

[b] Isolated yield based on aryl halide.

[c] The reaction was carried out in the presence of tetrabutylammonium bromide (1.3 mmol) using **2** (0.66 mmol).

[d] Tributyl(vinyl)tin (0.66 mmol) was used.

[e] Tributyl(phenyl)tin (0.87 mmol) was used.



Scheme 10.

Aryl bromides and triflate also underwent the cross-coupling, although a longer reaction time was required. Vinylation and phenylation of aryl iodide were also successful by use of tributyl(vinyl)tin and tributyl(phenyl)tin, respectively, in the presence of the palladium–iminophosphine catalyst.

3. Carbostannylation of alkynes

3.1. Introduction

Carbometalation of alkynes produces *cis*-substituted alkenylmetals and is an extremely useful method for a stereoselective olefin synthesis, since the resulting alkenylmetals can be transformed further to variously substituted ethylenes [15]. In particular, carbocupration [16], zirconium-catalyzed carboalumination [17] and nickel-catalyzed carbozincation [18] have a high synthetic potential due to wide applicability. Although alkenylstannanes are useful synthetic precursors for various olefinic targets [19], no report has been published on the transition metal-catalyzed carbostannylation of alkynes [20–22]. We envisaged that palladium complex **7** should react with alkynes to give carbostannylation products via carbopalladation or stannylpalladation. This turned out to be the case.

3.2. Carbostannylation

Treatment of tributyl(phenylethynyl)tin (**2**) with a 1:2 mixture of $[PdCl(\pi\text{-}C_3H_5)]_2$–IP (5 mol% of Pd) under an acetylenic atmosphere (1 atm) in THF at 50°C for 2 h gave tributyl[(*Z*)-2-(phenylethynyl)ethenyl]tin [23] in 81% yield [24] as a single isomer through an exclusive *syn*-addition (Scheme 10). The use of triphenylphosphine (two equivalents to palladium) in place of IP gave only 48% yield in a prolonged period (43 h) [25]. A Pd(0)–DPPP complex, which also was shown to be added oxidatively by **2**, was much less effective to give the carbostannylation product in 28% yield even after 22 h.

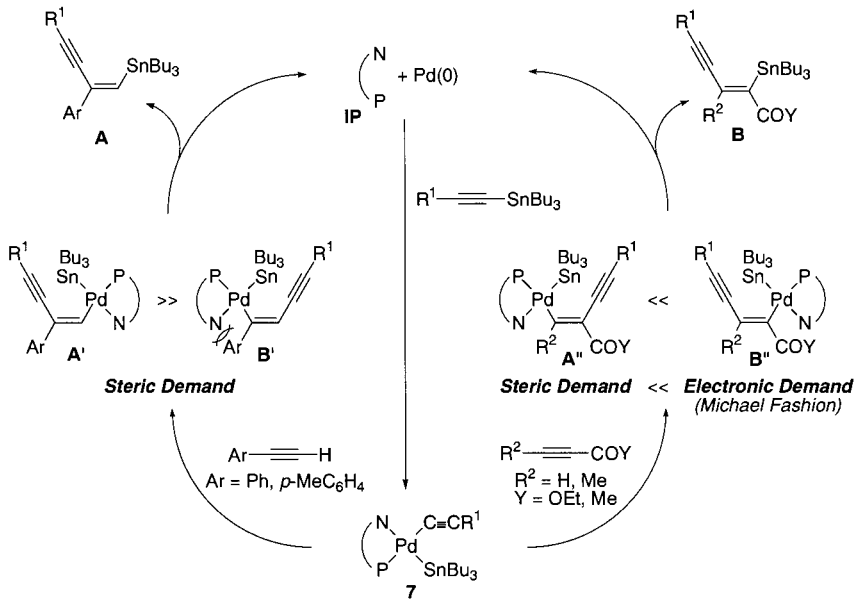
The carbostannylation of various alkynes catalyzed by the Pd–IP catalyst was next examined (Scheme 10, Table 2). The reaction of **2** with ethyl propiolate gave carbostannylation products consisting of regioisomers in a 20/80 ratio. The carbostannylation of ethyl 2-butynoate resulted in higher regioselectivity, though higher temperature and longer reaction time were required. A ketonic acetylene, 1-butyn-3-one, reacted with **2** smoothly with a regioselectivity similar to ethyl propiolate. The reaction of arylacetylenes with **2** was relatively slow to give the carbostannylation products in high yields but with a reversed regioselectivity. The reaction of ethoxyacetylene proceeded with high regioselectivity. Tributyl(1-hexyn-1-yl)tin also reacted with alkynes, giving the corresponding alkenylstannanes with the regioselectivity similar to **2** [26].

The catalytic cycle should first involve the oxidative addition of an alkynylstannane to the Pd(0) complex as discussed before. Successive insertion of an alkyne to

Table 2
Carbostannylation of alkynes with a Pd–IP catalyst[a]

R^1	R^2	R^3	Solvent	Temp (°C)	Time (h)	Yield[b] (%)	**A** : **B**[c]
Ph	H	H[d]	THF	50	2	81	–
	CO_2Et	H	THF	50	3	78	20 : 80
	CO_2Et	Me	Dioxane	90	90	57	1 : >99
	Ac	H	THF	50	4	76	15 : 85
	Ph	H	THF	50	21	81	92 : 8
	4-$CH_3C_6H_4$	H	THF	50	44	82	91 : 9
	EtO	H[e]	THF	50	5	52	>99 : 1
Bu	H	H[d]	THF	50	4	66	–
	CO_2Et	H	THF	50	16	72	12 : 88
	Ph	H	THF	50	29	80	92 : 8

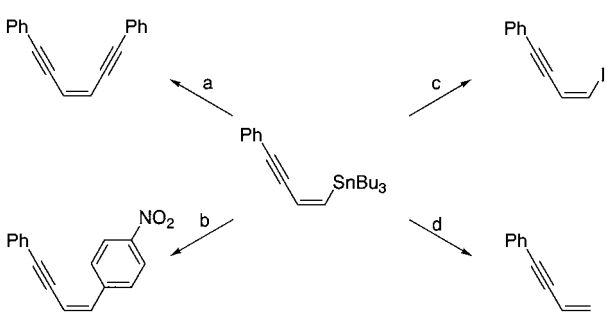
[a] The reaction was carried out in a solvent (5 ml) using an alkynylstannane (0.46 mmol) and an alkyne (1.38 mmol) in the presence of IP (0.022 mmol) and $[PdCl(\pi\text{-}C_3H_5)]_2$ (0.011 mmol).
[b] Isolated yield based on alkynylstannane.
[c] Determined by ^1H- or ^{119}Sn-NMR.
[d] The reaction was carried out under an acetylenic atmosphere (1 atm).
[e] Ethoxyacetylene (0.46 mmol) was used.



Scheme 11.

the C–Pd bond (carbopalladation) [27] of **7** followed by reductive elimination is likely to afford the carbostannylation product and regenerate the Pd(0) complex (Scheme 11). The opposite regioselectivity observed in use of arylacetylenes and alkynes having a carbonyl group can be explained by the following facts. In the cases of arylacetylenes, carbopalladation giving alkenylpalladiums would prefer **A′** to **B′** by a steric reason. Accordingly, alkenylstannanes **A** are produced as main products. In contrast, electron-deficient alkynes having a carbonyl group is likely to suffer the Michael addition of the alkynyl group giving **B** predominantly through **B″**.

Finally, the utility of the carbostannylation products is demonstrated by the transformation of the resulting (*Z*)-alkenyltin compounds (Scheme 12). For example, the Pd–tri(2-furyl)phosphine-catalyzed coupling [5] with 1-bromo-2-phenylethyne and 4-nitroiodobenzene [28] gave the respective coupled products in good yields. Iodolysis or hydrolysis afforded the corresponding alkenyl iodide or enyne in a good yield, respectively.



Scheme 12. (a) PhC≡CBr (0.92 equivalents), $Pd_2(dba)_3$, $(2\text{-furyl})_3P$ (5 mol% of Pd, $Pd/(2\text{-furyl})_3P = 1/4$), NMP, 50°C, 18 h, 58% (based on PhC≡CBr). (b) 4-$O_2NC_6H_4I$ (0.92 equivalents), $Pd_2(dba)_3$, $(2\text{-furyl})_3P$ (5 mol% of Pd, $Pd/(2\text{-furyl})_3P = 1/4$, toluene, 90°C, 13 h, 85% (based on 4-$O_2NC_6H_4I$). (c) I_2 (1.4 equivalents), THF, 0°C, 40 min, 92%. (d) Conc. HCl, THF, r.t., 1 h, 81%.

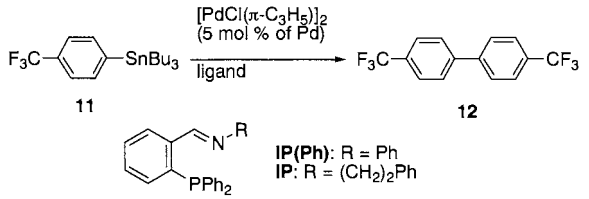
4. Homocoupling reaction of organostannanes

4.1. Introduction

The palladium-catalyzed homocoupling of organostannanes is much less familiar than the cross-coupling reaction. This may be ascribed to the fact that an appropriate re-oxidant of an intervening Pd(0) complex, making the homocoupling reaction catalytic, is additionally needed. Actually, all the examples of the palladium-catalyzed homocoupling of organostannanes [29] useful for organic synthesis [30] employs such an oxidant as *t*-BuOOH [31], benzoquinone [32], 1,2-dichloroethane [33], 2,3-dibromoacrylate [34] or 1,2-diiodoethene [35] except for the homocoupling of alkenylstannanes catalyzed by bis(acetonitrile)dichloropalladium(II) [36]. We have found that a palladium–iminophosphine complex efficiently catalyzes the homocoupling of organostannanes in the presence of such a mild and easily available oxidant as air [37] or allyl acetate.

4.2. Homocoupling reaction

The catalytic activity of a palladium complex coordinated by a phosphine-based ligand was examined in the homocoupling reaction of tributyl[4-(trifluoromethyl)-phenyl]tin (**11**) (Scheme 13). Yields of 4,4′-bis(tri-



Scheme 13.

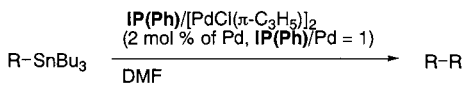
fluoromethyl)biphenyl (**12**) obtained after 4 h are summarized in Table 3. A palladium complex coordinated by *N*-(2-diphenylphosphinobenzylidene)aniline (**IP(Ph)**) showed higher reaction rate than any other palladium complexes examined. Thus, the reaction of **11** in *N*,*N*-dimethylformamide (DMF) in the presence of 5 mol% of Pd–**IP(Ph)** at 40°C for 4 h in open air gave over 95% yield of homocoupled product **12**. A palladium complex coordinated by IP was slightly less potent, giving **12** in 83%. Under the same reaction conditions, a palladium–triphenylphosphine complex (ligand/Pd = 2) gave **12** in 64% yield [38]. A palladium catalyst without any phosphine ligand was much less active, giving only 15% yield of **12**. The reaction under an argon atmosphere strictly set up gave **12** in < 5% yield, indicating that oxygen is essential for the homocoupling reaction [30a]. Kinetic experiments in various solvents show that DMF is the best solvent [39].

The Pd–**IP(Ph)** catalyst was applied to the homocoupling of a variety of aryl-, alkenyl- and alkynylstannanes (Scheme 14 and Table 4). In particular, arylstannanes reacted smoothly in the presence of 2

Table 3
Palladium-catalyzed homocoupling of **11**[a]

Ligand	Ligand/Pd	Solvent	Yield (%)[b] of **12**
IP(Ph)	1	DMF	>95 (87)[c]
IP	1	DMF	83
Ph_3P[d]	2	DMF	64
None	–	DMF	15
IP(Ph)[e]	1	DMF	<5
IP(Ph)	1	THF	30
IP(Ph)	1	Toluene	20
IP(Ph)	1	$CHCl_3$	16

[a] The reaction was carried out at 40°C for 4 h in a solvent (2 ml) in open air using **11** (0.32 mmol) in the presence of $[PdCl(\pi\text{-}C_3H_5)]_2$ (8.0 μmol) and a ligand (0.016 mmol).
[b] Determined by ^{19}F-NMR.
[c] Isolated yield is given in the parenthesis.
[d] Triphenylphosphine (0.032 mmol) was used.
[e] Under an argon atmosphere set up through three freeze-thaw cycles.



Scheme 14.

Table 4
Homocoupling of organostannanes with a Pd–IP(Ph) catalyst[a]

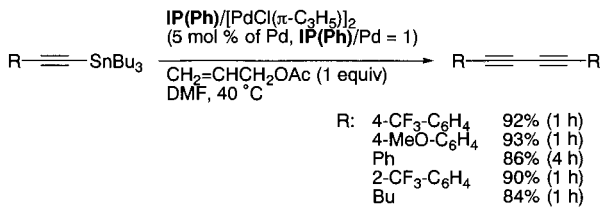
R in R–SnBu3	Temp (°C)	Time (h)	Yield (%)[b] of R–R
Ph	70	4	66
4-O_2N–C_6H_4	50	5	84
4-OHC–C_6H_4	50	36	76
4-MeO–C_6H_4	70	102	81
2-NC–C_6H_4	50	44	80
4-$HOCH_2$–C_6H_4	70	10	75
3-$MeOCO_2$–C_6H_4	50	2.5	60
2-Thienyl	50	53	60
2-Pyridyl	70	72	79
(*E*)-PhCH=CH[c]	50	4	68
PhC≡C	50	6	31
BuC≡C	50	11	34

[a] The reaction was carried out in DMF (2 ml) in open air using an organostannane (0.8 mmol) in the presence of $[PdCl(\pi\text{-}C_3H_5)]_2$ (8.0 μmol) and IP(Ph) (0.016 mmol).
[b] Isolated yield based on organostannane.
[c] (*E*,*E*)-1,4-Diphenylbutadiene was obtained.

mol% of the catalyst to give the corresponding biaryls in moderate to good yields, irrespective of the electron-withdrawing or -donating substituent on the phenyl ring. Heteroarylstannanes also gave homocoupled products in moderate to good yields. (*E*)-Tributyl(2-phenylethenyl)tin also underwent the oxidative dimerization in the presence of the Pd–IP(Ph) catalyst to give (*E*,*E*)-1,4-diphenyl-1,3-butadiene in 68% yield. Although alkynylstannanes reacted very fast, the expected products, 1,3-diynes, were isolated in yields less than 34%, probably due to the instability of the products under the reaction conditions.

During our investigation of the Pd–IP-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 the carbostannylation product. Therefore, we expected that allyl acetate should work effectively as an oxidant in the homocoupling of alkynylstannanes. This turned out to be the case.

The reaction of tributyl[4-(trifluoromethyl)phenylethynyl]tin with allyl acetate (1 equivalence) in the presence of 5 mol% of Pd–IP(Ph) in DMF for 1 h at 40°C gave 1,4-bis[4-(trifluoromethyl)phenyl]-1,3-butadiyne in > 95% yield (Scheme 15). The effect of



Scheme 15.

ligand and solvent on the catalytic activity was similar to that observed in the use of oxygen as an oxidant. It is worthy to note that allyl acetate does not react as a coupling partner of an alkynylstannane in spite of some reports on this topic [40].

Various alkynylstannanes were applied to the palladium-catalyzed homocoupling reaction using allyl acetate as an oxidant. Arylethynylstannanes generally gave the corresponding 1,3-diynes in good yields, irrespective of the kind of the substituent on the phenyl ring. 1-Hexyn-1-ylstannane was also reacted smoothly to give 5,7-dodecadiyne in a good yield.

5. Typical procedures

5.1. Cross-coupling reaction

A solution (5 ml) of IP (8.6 mg, 0.022 mmol), an aryl halide (0.44 mmol), and $[PdCl(\pi\text{-}C_3H_5)]_2$ (4.0 mg, 0.011 mmol) was degassed by three freeze-thaw cycles. To this solution was added an organostannane (0.48 mmol), and the mixture was stirred at the temperature indicated in Table 1. After the time specified in Table 1, a 1 M KF aqueous solution (2 ml) was added, and the reaction mixture was stirred at room temperature for 30 min. Filtration through a Celite pad was followed by extraction with ethyl acetate (50 ml). The organic layer was washed successively with water and brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by gel permeation chromatography gave the corresponding coupling product. The results are summarized in Table 1.

5.2. Carbostannylation of alkynes

A solution of IP (8.6 mg, 0.022 mmol), $[PdCl(\pi\text{-}C_3H_5)]_2$ (4.0 mg, 0.011 mmol), and an alkyne (1.38 mmol) in a solvent (5 ml) was degassed by four freeze–thaw cycles. To this solution was added an organostannane (0.46 mmol), and the mixture was stirred at the temperature indicated in Table 2. After the time specified in Table 2, the solvent was evaporated. Gel permeation chromatography of the residue gave the corresponding carbostannylation product. The results are summarized in Table 2.

5.3. Homocoupling reaction

5.3.1. With air as an oxidant

An organostannane (0.80 mmol) was added to a solution of IP(Ph) (6.0 mg, 0.016 mmol) and $[PdCl(\pi\text{-}C_3H_5)]_2$ (3.0 mg, 8 μmol) in DMF (2 ml), and the resulting mixture was stirred in open air at the temperature and the time indicated in Table 4. 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 results are summarized in Table 4.

5.3.2. With allyl acetate as an oxidant

An alkynylstannane (0.32 mmol) was added to a solution of allyl acetate (0.32 mmol), IP(Ph) (6.0 mg, 0.016 mmol) and $[PdCl(\pi\text{-}C_3H_5)]_2$ (3.0 mg, 8 μmol) in DMF (2 ml), and the resulting mixture was stirred at 40°C for the time depicted in Scheme 15. 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 Scheme 15.

6. Conclusions and prospect

The findings discussed herein will provide us with clues to further investigation concerning the coupling reaction of not only organostannanes but also other organometallic reagents. The novel catalytic cycle demonstrated here should work also in the cross-coupling reaction of other organometallic reagents.

The newly disclosed nucleophilic Pd(II) complex, (L–L′)Pd(R)(SnR'_3), will find wide applications leading to novel methodology for C–C bond forming reactions, as we disclosed the carbostannylation of alkynes.

Furthermore, the electrophilic Pd(0) complex discussed herein will also open its own future by reacting with various nucleophilic reagents other than organostannanes.

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