

Sequential Photostimulated Reactions of Trimethylstannyl Anions with Aromatic Compounds Followed by Palladium-Catalyzed Cross-Coupling Processes

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The photostimulated reactions of several mono-, di-, and trichloroarenes and aryltrimethylammonium salts with Me_3Sn^- ions in liquid ammonia gave good yields of stannanes by the $\text{S}_{\text{RN}}1$ mechanism. If the chloroarenes are not soluble in liquid ammonia, diglyme is another solvent to perform these reactions. The stannanes thus obtained can be arylated by further reaction with haloarenes through palladium-catalyzed reactions. If the palladium-catalyzed reaction is performed with a chloriodoarene as substrate, the stannane reacts faster by the C–I bond via chemoselective cross-coupling reaction to give a chloroarene as product, which can be further arylated by a consecutive $\text{S}_{\text{RN}}1$ –Stille reaction or react with other substrates by another palladium-catalyzed reaction. These sequential reactions can also be performed with substrates with two leaving groups to give products in high yields.

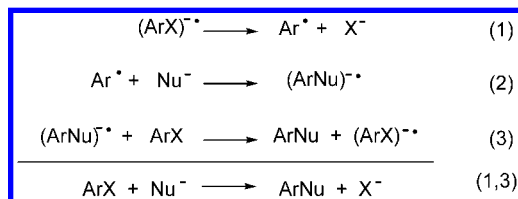
Introduction

The radical nucleophilic substitution, or $\text{S}_{\text{RN}}1$ reaction, is a chain process through which an aromatic nucleophilic substitution is obtained. The scope of the process has considerably increased, and nowadays, it is an important synthetic possibility to achieve substitution of different substrates.¹ Several nucleophiles can be used such as carbanions and anions from compounds bearing heteroatoms, which react to form new C–C or C–heteroatom bond in good yields. Many substituents are compatible with the $\text{S}_{\text{RN}}1$ mechanism such as CO_2^- , CO_2R , CONR_2 , RO^- , CN , R , aryl, NH_2 , NR_2 , and SO_2R . Substituents such as $-\text{O}^-$ or $-\text{NO}_2$ are not suitable except when arylazo phenyl sulfides are used as substrates.¹

This chain process requires an initiation step. In a few systems, spontaneous electron transfer (ET) from the nucleophile to the substrate has been observed. When the ET does not occur spontaneously, it can be induced by light stimulation.¹ The propagation steps of $\text{S}_{\text{RN}}1$ mechanism are presented in Scheme 1. Overall, eqs 1–3 depict a nucleophilic substitution (eq 1,3) in which radicals and radical anions are intermediates.

The reaction of triorganostannyl ions as nucleophiles with aryl halides has long been known, and the products obtained depend on the leaving group, nucleophile, solvent, and reaction conditions.² We have described the photostimulated reactions of trimethylstannyl ions (Me_3Sn^-) with several chloroarenes in liquid ammonia

Scheme 1



that afforded ArSnMe_3 in very good to excellent yields (70–100%).³ The fact that there is no reaction in the dark but only under irradiation and that the photostimulated reactions are inhibited by *p*-dinitrobenzene (*p*-DNB), a well-known inhibitor of $\text{S}_{\text{RN}}1$ reactions, indicates that these reactions occur by the $\text{S}_{\text{RN}}1$ mechanism. These reactions are an alternative route to the synthesis of stannanes, avoiding the use of Grignard reagents or organolithium compound. These reactions can also be carried out in DMSO as solvent under irradiation.⁴

The $\text{S}_{\text{RN}}1$ reactions of dihaloarenes with nucleophiles afford either the monosubstitution or disubstitution product, depending on the structure of the substrate, the nature of the nucleofugal group, or the nucleophile.¹ We found that several dichloroarenes and dichloropyridines give the disubstitution product in high yield and that the photostimulated reaction of 1,3,5-trichlorobenzene in the presence of an excess of Me_3Sn^- ion affords 71% of the trisubstitution product.⁵ Mono- and distannanes can also be formed from diethylaryl phosphonates⁶ or aryltrimethylammonium salts⁷ by the $\text{S}_{\text{RN}}1$ mechanism.

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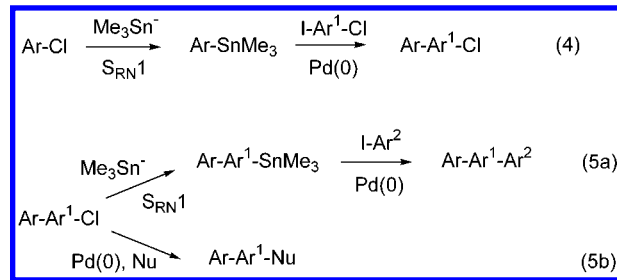
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For more than a decade, the palladium-catalyzed coupling of organotin compounds with carbon electrophiles, known as the Stille reaction,⁸ has been shown to be a very important tool in organic synthesis.⁹ Another approach to the synthesis of aryltrialkylstannanes is the palladium-catalyzed cross-coupling reaction of aryl halides¹⁰ or aryl triflates¹¹ with hexamethyl- and hexabutyldistannanes. Bis(trimethylstannyl) arenes can also be synthesized by the palladium-catalyzed reactions; thus, the reaction of 3,5-dibromobiphenyl with hexamethyldistannane gave 90% yield of the ditin product; other examples yielded 40–60% disubstitution.¹² There are few examples involving reactions of bis(trimethylstannyl)-arenes and -heteroarenes with aryl halides, which afford a double arylation by the palladium cross-coupling reaction. The examples are known afford modest to good yields (6–85% yield) of double arylation.¹³

The stannanes obtained by the $S_{RN}1$ mechanism reacted by a palladium-catalyzed cross-coupling reaction with halobenzenes to give phenylated products also in very good yields.¹⁴ For instance, *m*- and *p*-bis(trimethylstannanyl)benzenes obtained by the $S_{RN}1$ mechanism react with iodobenzene in a cross-coupling reaction catalyzed by palladium to afford *m*- and *p*-terphenyls in high yields. Similarly, 1,3,5-tris(trimethylstannanyl) benzene, upon treatment with iodobenzene and palladium, furnished 1,3,5-triphenylbenzene in 89% yields.¹⁴ This is the first report of a trisubstitution by a cross-coupling reaction catalyzed by palladium. Similar yields can be obtained in one-pot reactions.¹⁴

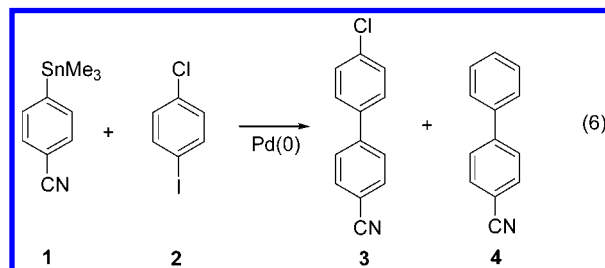
The fact that chloroarenes react with Me_3Sn^- ions under irradiation to form aryltrimethylstannanes and that in the palladium-catalyzed reaction with stannanes the reactivity of iodoarenes is much greater than that of chloroarenes, a substrate bearing both leaving groups, chlorine and iodine, will react faster by the C–I bond (product $Ar-Ar^1-Cl$, eq 4) in a cross-coupling reaction with a stannane catalyzed by palladium. This will allow the remainder leaving group, chlorine, to react later in another $S_{RN}1$ -type of reaction to form an organostannyl intermediate (product $Ar-Ar^1-SnMe_3$ (eq 5a), which can ultimately furnish product $Ar-Ar^1-Ar^2$ (eq 5a) by a cross-coupling palladium-catalyzed reaction. Or else, the product obtained in eq 4 by another palladium-catalyzed reaction with a substrate Nu may furnish the product of eq 5b.



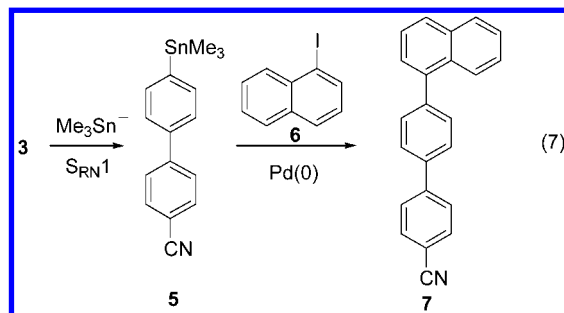
The reactions of the above sequences were investigated in order to foster a methodology to build large molecules and to know the scope and the limitations of this synthetic strategy, with chloro- and dichloroarenes as substrates.

Results and Discussion

The photostimulated reaction of *p*-chlorobenzonitrile with Me_3Sn^- ions in liquid ammonia affords the stannane **1** (94%, 85% isolated yield).⁵ The reaction of **1** with PhI and $Pd(PPh_3)_2Cl_2$ as catalyst in DMF affords the coupling product biphenyl-4-carbonitrile in 81% yield.¹⁴ When a solution of **1**, *p*-chloriodobenzene (**2**), and $Pd(PPh_3)_2Cl_2$ in DMF was heated to 80 °C for 3 h, the substitution product **3** (72%) and the dechlorinated product **4** (25%) were obtained (eq 6). Product **4** is formed by the phenyl–chlorophenyl ring exchange between the palladium center and phosphine ligands in the palladium(II) complexes.¹⁵ When the catalyst was in only 2 mol % under the same experimental conditions, the yield of **3** increases up to was 91%, and no product **4** was found (Table 2, entries 1 and 2).



The photostimulated reaction of **3** and Me_3Sn^- ions in liquid ammonia afforded stannane **5** in 94% yield (eq 7) (Table 1, entry 1). When the stannane **5** thus obtained was allowed to react with 1-iodonaphthalene (**6**) and $Pd(PPh_3)_2Cl_2$ in DMF (80 °C, 4 h), product **7** was obtained in high yields (eq 7) (Table 2, entry 3).



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Table 1. Reactions of Chloroareenes and Related Substrates with Me₃Sn[−] Ions

entry	substrate (mmol)	Me ₃ Sn [−] (mmol)	solvent ^a	conditions (min)	Cl [−] %	substitution product ^b (%)
1	3 (0.52)	0.62	NH ₃	<i>hν</i> (110)	98	94
2	9 (1.00)	2.20	NH ₃	<i>hν</i> (120)	17	<i>c</i>
3	<i>p</i> -NCC ₆ H ₄ Cl (1.00)	4.00	diglyme	dark (60)		
4	<i>p</i> -NCC ₆ H ₄ Cl (1.00)	4.00	diglyme	<i>hν</i> (60)	94	70 ^d
5	1-ClC ₁₀ H ₇ (1.50)	6.00	diglyme	dark (40)		
6	1-ClC ₁₀ H ₇ (1.50)	6.00	diglyme	<i>hν</i> (40)	98	88 ^e
7	<i>m</i> -Cl ₂ C ₆ H ₄ (1.10)	8.80	diglyme	dark (60)		
8	<i>m</i> -Cl ₂ C ₆ H ₄ (1.10)	8.80	diglyme	<i>hν</i> (60)	94 ^f	85 ^g
9	1,3,5-Cl ₃ C ₆ H ₃ (0.40)	6.00	diglyme	dark (140)		
10	1,3,5-Cl ₃ C ₆ H ₃ (0.40)	6.00	diglyme	<i>hν</i> (140)	95 ^h	28 ⁱ
11	9 (0.60)	4.80	diglyme	dark (120)	11 ^f	11 , 4 ^j
12	9 (0.60)	4.80	diglyme	<i>hν</i> (90)	97 ^f	11 , 79 ^k
13	PhNMe ₃ I (1.00)	2.20	NH ₃	dark (50)	1	40
14	PhNMe ₃ I (1.00)	2.20	NH ₃	dark (50) ^m	1	
15	PhNMe ₃ I (1.00)	2.20	NH ₃	<i>hν</i> (50)	1	98
16	14 (0.40)	1.00	NH ₃	<i>hν</i> (90)	1	11 , 83 ⁿ
17	<i>p</i> -NH ₂ C ₆ H ₄ Cl (1.13)	3.88	NH ₃	<i>hν</i> (180)	100	95

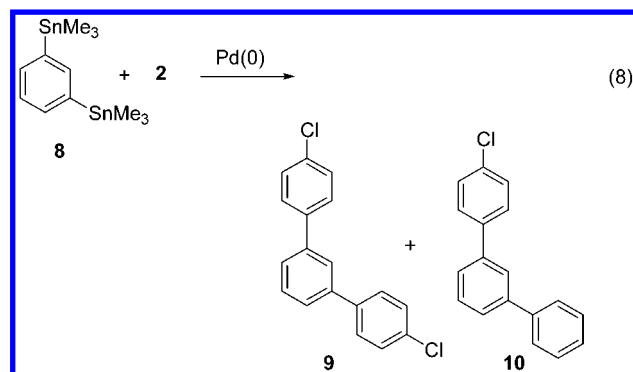
^a The reactions were performed in diglyme (20 mL) and liquid ammonia (250 mL). ^b Determined by GLC, unless otherwise indicated. ^c Detected in a small amount but not quantified. ^d C₆H₅CN was detected but not quantified. ^e Naphthalene was obtained in 10% yield. ^f Considering two chlorines per molecule. ^g Disubstitution product. ^h Considering three chlorines per molecule. ⁱ Trisubstitution product together with 60% yield of the disubstitution product **8**. ^j Product **12** in 3% yield. ^k Product **12** in 11% yield. ^l Not quantified. ^m *p*-DNB (23 mol %) was added. ⁿ Product **12** in 4% yield.

Table 2. Palladium-Catalyzed Cross-Coupling Reaction of Mono- and Distannanes and Diphenylamine with Electrophiles in DMF^a

entry	substrate (mmol)	electrophile (mmol)	Pd(PPh ₃) ₂ Cl ₂ (mol %)	time (h) (T (°C))	products (yield, %) ^b
1	1 (1.50)	2 (1.50)	5.0	3 (80)	3 (72), 4 (25)
2	1 (1.50)	2 (1.50)	2.0	3 (80)	3 (91), 4 (>1)
3	5 (0.16)	6 (0.20)	5.0	4 (80)	7 (94)
4	8 (0.56)	2 (1.15)	2.0	1.5 (80)	9 (55), 10 (25)
5	8 (0.56)	2 (2.27)	1.3	1.5 (80)	9 (73), 10 (9)
6	8 (0.56)	2 (2.27)	1.0	1.5 (80)	9 (84), 10 (5)
7	8 (0.56)	13 (1.12)	2.2 ^c	10 (80)	14 (84) ^d
8	11 (0.10)	6 (0.50)	5.0	8 (80)	17 (81) ^d
9	18 (1.20)	9 (0.50)	2.9 ^e	14 (80)	19 (74) ^d

^a In 20 mL of DMF. ^b Determined by GLC, unless otherwise indicated. ^c The catalyst was Pd₂(dba)₃, with Ph₃As (16.1 mol %) as ligand and CuI (10.0 mol %) as cocatalyst. The solvent was 90 mL of DMSO. ^d Isolated yield. ^e The catalysts were Pd₂(dba)₃, with (*o*-biphenyl)P(*t*-Bu)₂ (5.3 mol %) as ligand and *t*-BuOK (1.60 mmol). The solvent was 5 mL of toluene.

The photostimulated reaction of *m*-dichlorobenzene and Me₃Sn[−] ions in liquid ammonia afforded the distannane **8** in 90% yield.⁵ When the distannane **8** was allowed to react with **2** and the catalyst Pd(PPh₃)₂Cl₂ in DMF, the disubstitution product **9** and the product with only one chlorine **10** were obtained in variable yields, depending on the ratio of **8** and **2** and the amount of the catalysts (eq 8). When the ratio of **8**:**2** was 1:4 and 1.0 mol % of the catalysts, the yield of **9** increased up to 84% and only 5% yield of **9** was obtained (Table 2, entries 4–6).



Compound **9** was completely insoluble in liquid ammonia and did not react with Me₃Sn[−] ions under irradiation (Table 1, entry 2).

It is known that haloarenes and haloheteroarenes react with Me₃Sn[−] ions in 1,2-dimethoxyethane (DME), di-

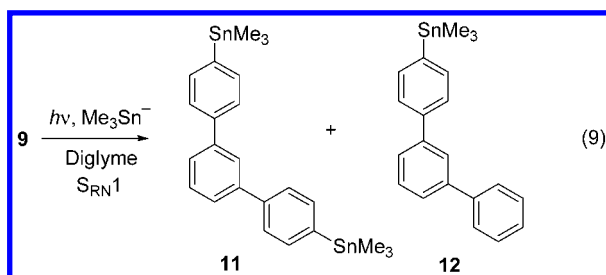
glyme, and tetraglyme as solvent to yield the substitution product, but no mechanistic studies have been performed. There is a report of the reactions of chloro-, bromo-, dichloro-, and dibromopyridines with Me₃Sn[−] ions in DME to afford the substitution products (60–88%).¹⁶ Musfeldt et al. prepared *m*- and *p*-bis(trimethylstannyl)benzene by the reaction of *m*- and *p*-diiodobenzene with NaSnMe₃ in diglyme and benzene as solvents (62–65%).¹⁷ Wursthorn and Kuivila reported that the reaction of *o*-dibromobenzene with NaSnMe₃ in tetraglyme afforded the disubstitution product in 42% yield.¹⁸ A series of 1,2-distannylated aromatics and heteroaromatics was prepared by treating the dibromo precursors with NaSnMe₃ in tetraglyme.¹⁹ No light was used to induce these reactions.

There is no reaction of *p*-chlorobenzonitrile or 1-chloronaphthalene in the dark with Me₃Sn[−] ions in diglyme, but under irradiation it gives 70% and 88% yields of the substitution products (Table 1, entries 3–6), lower yields as in the reaction in liquid ammonia (85% and 90% yields, respectively). *m*-Dichlorobenzene did not react in the dark with Me₃Sn[−] ions in diglyme, but under irradiation the yield of the disubstitution product was 85% (Table

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1, entries 7 and 8), a slightly lower yield compared with the reaction in liquid ammonia (90% yield). The reaction of 1,3,5-trichlorobenzene with Me_3Sn^- ions in liquid ammonia afforded 71% of the trisubstitution product; however, only 28% yield was obtained in the photoinitiated reaction in diglyme, together with 60% yield of the disubstitution product **8** (Table 1, entries 9 and 10). All these results indicate that in diglyme as solvent, the yields are lower compared with liquid ammonia. With one or two leaving groups, the yields are slightly lower, and with three leaving groups the yields are low compared with the reactions in liquid ammonia. These results show that the reduction process is more important in diglyme than in liquid ammonia.

There is a slow dark reaction of **9** with Me_3Sn^- ions in diglyme, but under irradiation the disubstitution product **11** is obtained in 79% yield, and the monosubstitution product **12** in 11% yield (eq 9) (Table 1, entries 11 and 12). This result indicates that diglyme is a suitable solvent for the photoinduced $\text{S}_{\text{RN}}1$ reactions with Me_3Sn^- ions.

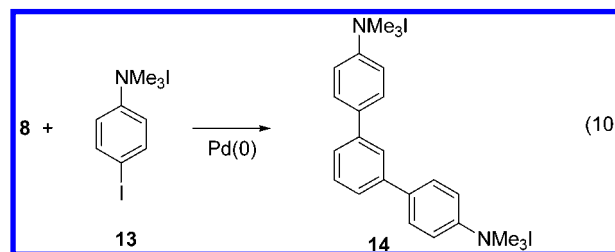


We studied the synthesis of **11** by another route, changing the leaving group chlorine by trimethylammonium iodide. These salts are quite soluble in liquid ammonia. It is known that trimethylammonium can act as a leaving group in $\text{S}_{\text{RN}}1$ reactions.²⁰ It can be seen in Table 1 (entries 13–15) that there is a slow reaction of phenyltrimethylammonium iodide with Me_3Sn^- ions in the dark, reaction that is completely inhibited by *p*-DNB. Under irradiation, the substitution product trimethylphenylstannane is obtained in 98% yield. These results indicate that trimethylammonium salts are very good substrates in $\text{S}_{\text{RN}}1$ reactions with Me_3Sn^- ions.

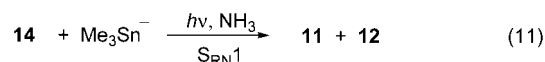
The palladium-catalyzed reaction of stannanes with haloarenes substituted with the amino group gave low yields or no reaction. It is known that the amino group slows down the oxidative addition of palladium(0).⁹ For instance, *p*-iodoaniline gave 57% in a cross-coupling reaction with a stannane,²¹ but *p*-iodo-*N,N*-dimethylaniline failed to react.²²

Stannane **8** with *p*-iodoaniline did not give the expected substitution product in a palladium-catalyzed cross-coupling reaction. As far as we know, there is no example of a trialkylammonium salt as substituent in the haloarene in cross-coupling reactions catalyzed by palladium. We thought that this group may facilitate the oxidative addition. In the palladium-catalyzed reaction of stannane **8** with *p*-iodophenyltrimethylammonium iodide (**13**), the

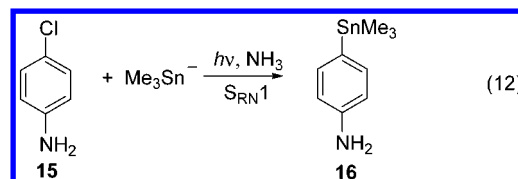
disubstitution product **14** is obtained in 84% yield (Table 2, entry 7) (eq 10).



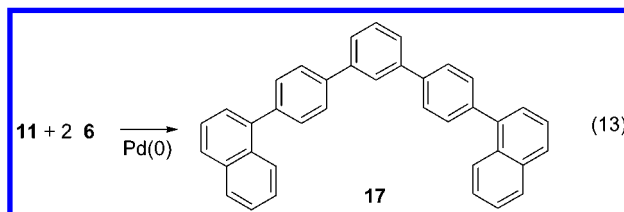
Compound **14** was soluble in liquid ammonia, and in the photostimulated reaction with Me_3Sn^- ions, compounds **11** and **12** were obtained in 83% and 4% yields, respectively (eq 11) (Table 1, entry 16).



As the trimethylammonium is a good leaving group in $\text{S}_{\text{RN}}1$ reactions, it was of interest to know if a chloroarene with an amino group reacts with Me_3Sn^- ions by this mechanism. The amino group as substituent in the aromatic moiety did not interfere in the reaction with some nucleophiles, but inhibited or gave low yields with others.¹ For instance, *p*-bromo-*N,N*-diethylamine did not react with pinacolone enolate anions under irradiation in liquid ammonia,²³ but good yields of products are obtained in the reaction of *o*-haloanilines and derivatives with carbanions to obtain indoles.²⁴ *o*-Iodoaniline gives only 10% of substitution with benzenethiolate ions.²⁵ The photostimulated reaction of *p*-chloroaniline with Me_3Sn^- ions in liquid ammonia afforded high yields (95%) of the substitution product **16** (eq 12) (Table 1, entry 17).



When the distannane **11** was allowed to react with **6** in a cross-coupling reaction catalyzed by palladium, the hydrocarbon **17** was obtained (81%) (Table 2, entry 8) (eq 13).



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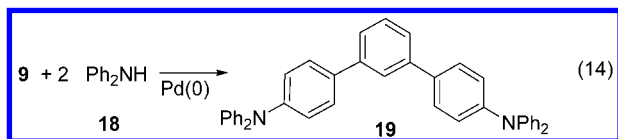
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It is known that aryl chlorides can react with amines with different palladium catalysts and ligands,²⁶ such as $Pd_2(dba)_3$ and (*o*-biphenyl)-P(*t*-Bu)₂ as ligand.²⁷ When **9** is treated with this catalyst system and diphenylamine **18** as substrate, product **19** was obtained in 74% yield (Table 2, entry 9) (eq 14).



Conclusions

These findings confirm the conclusions that the $S_{RN}1$ mechanism is an excellent method to obtain stannanes by the photostimulated reactions of mono-, di-, and trichloroarenes with Me_3Sn^- ions, in liquid ammonia, or if the chloroarenes are not soluble, diglyme is another solvent to perform these reactions. The stannanes thus obtained can be arylated by further reaction with bromo or iodoarenes through palladium-catalyzed reactions. Another conclusion that emerges from these results is that the product obtained with a chloriodoarene is another aryl chloride that can be further transformed into a stannane to give ultimately, by a Pd-catalyzed reaction, the final product of this sequence. Thus, this sequence can be successfully applied to build large molecules.

Experimental Section

Materials. *p*-Chlorobenzonitrile, *p*-chloriodobenzene, *m*-dichlorobenzene, *p*-iodoaniline, 1-iodonaphthalene, diphenylamine, and trimethylstannyl chloride were commercially available and used as received. *p*-Iodophenyltrimethylammonium iodide (90%) was obtained from the reaction of *p*-iodoaniline and methyl iodide in excess in DMF and 2-methylpyridine by the standard procedure described in the literature;²⁸ white solid, mp 193–195 °C dec (lit.²⁹ mp 196–198 °C dec). Diglyme was treated with pellets of NaOH (1 day), was refluxed with sodium metal (4–5 h), was vacuum distilled under nitrogen atmosphere, and finally stored with sodium wires under nitrogen in the dark.

Photostimulated Reaction of Me_3Sn^- ions in Liquid Ammonia. Irradiation was conducted in a reactor equipped with two 250-W UV lamps emitting maximally at 350 nm (water-refrigerated). The following procedure of the reaction of 4'-chlorobiphenyl-4-carbonitrile (**3**) with Me_3Sn^- ions is representative of all the reactions. Into a three-necked, 500-mL, round-bottomed flask equipped with a coldfinger condenser charged with dry ice–ethanol, a nitrogen inlet, and a magnetic stirrer was condensed 250 mL of ammonia previously dried with sodium metal under nitrogen. The Me_3SnCl (0.62 mmol) and sodium metal (1.30 mmol) were added. To this solution was added 0.52 mmol of **3**, and the mixture was irradiated for 110 min. The reaction was quenched by addition of NH_4NO_3 in excess, and the ammonia was allowed to evaporate. The residue was dissolved with water and then extracted with diethyl ether. The chloride ions in the aqueous solution were determined potentiometrically. The product was quantified by GLC using the internal standard method.

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Photostimulated Reaction of Me_3Sn^- Ions in Diglyme.

The photostimulated reaction of 1-chloronaphthalene with Me_3Sn^- ions is representative of all the reactions. The Me_3Sn^- ions (6.00 mmol) were prepared in liquid ammonia with the procedure described before, and the ammonia was allowed to evaporate. To the residue was added 20 mL of diglyme, and 1-chloronaphthalene (1.50 mmol) was added and irradiated for 40 min at ca. 0 °C. The reaction was quenched by addition of an aqueous solution of NH_4NO_3 in excess and extracted with diethyl ether. The chloride ions in the aqueous solution were determined potentiometrically. The ether extract was washed twice with water and dried, and the product was quantified by GLC with the internal standard method compared with an authentic sample.³

Cross-Coupling Reaction of **1** with **2** Catalyzed by Pd-

(PPh₃)₂Cl₂. The following procedure is representative of all the reactions. Into a three-necked, 50-mL, round-bottomed flask equipped with a condenser, a nitrogen inlet, and a magnetic stirrer was added 20 mL of DMF and then the stannane **1** (1.50 mmol), **2** (1.50 mmol), and the catalyst (0.03 mmol, 2 mol %), and the solution was heated to 80 °C for 3 h. The solution was filtered, water (50 mL) was added, and then the solution was extracted three times with diethyl ether. The product was quantified by GLC using the internal standard method compared with authentic samples. Products were **3** and **4** isolated by column chromatography on silica gel (eluent: petroleum ether/diethyl ether 75:25), and their spectroscopic data agreed with those reported in the literature. Compound **4** was compared with an authentic sample.¹⁴ Compound **3**: MS (*m/z*, rel int) 215 (34, $M^+ + 2$), 213 (100, M^+), 178 (13), 177 (20), 151 (25), 75 (23); white solid; mp 124–126 °C (lit.³⁰ mp 123–125 °C).

Isolation and Identification of the Products. 4'-Trimethylstannanylbiphenyl-4-carbonitrile (5**).** Compound **5** was purified by column chromatography on silica gel (eluent: petroleum ether/diethyl ether 70:30): white solid; mp 94–96 °C; ¹H NMR (200.13 MHz; CDCl₃/Me₄Si) δ 0.34 (s, 9 H, ²J(¹¹⁷–¹¹⁹SnCH) = 53.0, 55.2 Hz), 7.51–7.79 (m, 8 H); ¹³C NMR (50.288 MHz; CDCl₃) δ (¹¹⁹Sn–¹³C) –2.48, 110.90, 118.93, 126.67 (44.72 Hz, C₂), 127.69, 132.60, 136.56 (36.59 Hz, C₃), 138.99, 143.41, 145.75; MS (EI, *m/z*, rel int) 343 (2, M^+), 328 (100, $M^+ - CH_3$), 298 (34), 179 (7), 152 (11). Anal. Calcd. for C₁₆H₁₇NSn: C, 56.19; H, 5.01; N, 4.10; Sn, 34.70. Found: C, 56.68; H, 5.42; N, 4.07.

4'-Naphthalen-1-ylbiphenyl-4-carbonitrile (7**).** Compound **7** was purified by column chromatography on silica gel (eluent: petroleum ether/diethyl ether 95:5): white solid; mp 159–161 °C; ¹H NMR (200.13 MHz; CDCl₃; Me₄Si) δ 7.38–7.57 (m, 8 H), 7.69–7.94 (m, 7 H); ¹³C NMR (50.288 MHz; CDCl₃) δ 111.34, 119.24, 125.75, 126.06, 126.22, 126.54, 127.27, 127.43, 128.00, 128.35, 128.73, 131.15, 131.80, 132.98, 134.17, 138.32, 139.64, 141.64, 145.62; MS (EI, *m/z*, rel int) 305 (100, M^+), 304 (41), 278 (2), 203 (15), 202 (17), 178 (1), 152 (33), 102 (3); HRMS (EI) calcd for C₂₃H₁₅N 305.12045, found 305.12048.

4,4'-Dichloro-[1,1';3',1'']terphenyl (9**).** Compound **9** was purified by column chromatography on silica gel (eluent: petroleum ether): white solid; mp 114–116 °C; ¹H NMR (200.13 MHz; CDCl₃; Me₄Si) δ 7.38–7.68 (m, 11 H), 7.72 (s, 1 H); ¹³C NMR (50.288 MHz; CDCl₃) δ 125.75, 126.26, 128.47, 129.01, 129.44, 133.70, 139.44, 140.74; MS (EI, *m/z*, rel int) 301 (11, $M^+ + 2$), 300 (63, $M^+ + 1$), 299 (17), 298 (100), 264 (3), 262 (7), 228 (27), 226 (25), 150 (12). Anal. Calcd for C₁₈H₁₂Cl₂: C, 72.26; H, 4.04; Cl, 23.70. Found: C, 72.20; H, 4.29.

4,4'-Bis(trimethylstannanyl)[1,1';3',1'']terphenyl (**11**).

Compound **11** was purified by column chromatography on silica gel (eluent: petroleum ether): white solid; mp 82–84 °C; ¹H NMR (200.13 MHz; CDCl₃; Me₄Si) δ 0.33 (s, 18 H, ²J(¹¹⁹SnCH) = 54.6 Hz), 7.35–7.78 (m, 11 H), 7.82 (s, 1 H); ¹³C NMR (50.288 MHz; CDCl₃) δ –2.12, 126.46, 127.19 (46.08 Hz, C_{2,2'}), 129.13, 129.51, 136.65 (36.59 Hz, C_{3,3'}), 141.45, 141.66, 142.17; MS (EI, *m/z*, rel int) 496 (3, $M^+ - 4 CH_3$), 481 (33),

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466 (20), 348 (31), 263 (100), 247 (85), 232 (72), 228 (40), 152 (9); HRMS (EI) calcd for $C_{23}H_{27}^{118}Sn^{120}Sn$ ($[M - CH_3]^+$) 540.9678, found 540.9679.

4-(Trimethylstannanyl)phenylamine (16). Compound **16** was vacuum distilled using a Kugelrohr apparatus, and the spectroscopic data agreed with those reported in the literature:¹⁸ 1H NMR (200.13 MHz; $CDCl_3$; Me_4Si) δ 0.19 (s, 9 H, 2J ($^{119}SnCH$) = 53.0 Hz), 3.53 (s, 2 H), 6.41–7.05 (m, AA'BB'system, 4 H).

4,4'-Dinaphthalen-1-yl[1,1';3',1'']terphenyl (17). Compound **17** was purified by column chromatography on silica gel (eluent: petroleum ether): white solid; mp 163–165 °C; 1H NMR (200.13 MHz; $CDCl_3$; Me_4Si) δ 7.16–7.48 (m, 15 H), 7.63–7.98 (m, 11 H); MS (EI, m/z , rel int) 483 (46, $M^+ + 1$), 482 (73, M^+), 356 (1), 352 (2), 241 (100), 226 (5), 203 (31), 202 (33), 152 (2). Anal. Calcd for $C_{38}H_{26}$: C, 94.57; H, 5.43. Found: C, 94.25; H, 5.74.

Cross-Coupling Reaction of 8 with 13 Catalyzed by $Pd_2(dba)_3$. Into a three-necked, 250 mL, round-bottomed flask equipped with a condenser, a nitrogen inlet, and a magnetic stirrer were added 90 mL of DMSO followed by stannane **8** (0.56 mmol), *p*-iodophenyltrimethylammonium iodide (**13**) (1.12 mmol), the catalyst system $Pd_2(dba)_3$ (0.025 mmol, 2.2 mol %), Ph_3As (0.180 mmol 16.1 mol %), and CuI (0.112 mmol, 10.0 mol %). This solution was heated to 80 °C for 10 h. The solution was filtered, and DMSO was distilled. The residue was recrystallized from methanol to give **14** in 84% yield. **4,4''-Bis(trimethylammonium)[1,1';3',1'']terphenylbenzene diiodide (14):** whitish solid; mp 116–118 °C dec; 1H NMR (200.13 MHz; $DMSO-d_6$; Me_4Si) δ 3.71 (s, 18 H), 6.22 (d, 4 H, J = 7.7 Hz), 6.95 (d, 4 H, J = 7.3 Hz), 7.28–7.65 (m, 3 H), 8.29 (s, 1 H); MS (EI, m/z , rel int) 316 (100, $M^+ - 2 CH_3I$), 301 (11), 285 (5), 270 (2), 253 (11), 228 (8); HRMS (EI) calcd for $C_{22}H_{24}N_2$ ($[M - 2 CH_3I]^+$) 316.0369, found 316.0380. Anal. Calcd for $C_{24}H_{30}I_2N_2$: I, 42.28. Found: I, 41.7 (determined potentiometrically).

Cross-Coupling Reaction of 9 with 18 Catalyzed by $Pd_2(dba)_3$. Into a three-necked, 25 mL, round-bottomed flask equipped with a condenser, a nitrogen inlet, and a magnetic stirrer were added 5 mL of toluene followed by substrate **9** (0.50 mmol), $HNPh_2$ (**18**) (1.20 mmol), the catalyst system $Pd_2(dba)_3$ (0.029 mmol, 2.9 mol %), *o*-biphenyl- $P(t-Bu)_2$ (0.053 mmol, 5.3 mol %), and the base *t*-BuOK (1.60 mmol). The solution was heated to 80 °C for 14 h. After that, the solution was filtered, water (40 mL) was added, and then the solution was extracted three times with diethyl ether. The product **19** was purified by column chromatography on silica gel (eluent: petroleum ether/diethyl ether 50:50). It was rendered in 74% yield. ***N,N,N',N'*-Tetraphenyl[1,1';3',1'']terphenyl-4,4''-diamine (19):** white solid; mp 131–133 °C; 1H NMR (200.13 MHz; $CDCl_3$; Me_4Si) δ 6.82–7.09 (m, 12 H), 7.20–7.31 (m, 12 H), 7.35–7.59 (m, 7 H), 7.71 (s, 1H); ^{13}C NMR (50.288 MHz; $CDCl_3$) δ 117.85, 121.01, 122.95, 123.92, 124.46, 125.21, 127.88, 129.28, 135.19, 141.20, 147.32, 147.72; MS (EI, m/z , rel int) 566 (71, $M^+ + 2$), 565 (100, $M^+ + 1$), 564 (49), 397 (1), 283 (4), 244 (2), 168 (5); HRMS (EI) calcd for $C_{42}H_{32}N_2$ 564.2565, found 564.2568. Anal. Calcd for $C_{42}H_{32}N_2$: C, 89.33; H, 5.71; N, 4.96. Found: C, 88.92; H, 5.09.

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Supporting Information Available: ^{13}C NMR of compounds **5**, **7**, **9**, **11**, and **19**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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