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Highly Selective Cross-Coupling Reactions of Aryl(halo)silanes with Aryl Halides: A General and Practical Route to Functionalized Biaryls

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Abstract: *The palladium catalyzed cross-coupling reaction of aryl halides with aryl(halo)silanes (halogen= F, Cl) gives good yields of unsymmetrical biaryls and p-terphenyls. The reaction takes place smoothly in N,N-dimethylformamide in the presence of an appropriate palladium catalyst and potassium fluoride. Since this reaction is tolerant of a variety of reactive functional groups, highly functionalized 4,4'-, 3,4'-, 2,4'- and even sterically crowded 2,2'-disubstituted biaryls can be obtained in moderate to high yields. The synthetic utility of the method has been demonstrated by its application to a short synthesis of liquid crystals. Mechanistic aspects of transmetalation of an aryl(fluoro)silicate intermediate with a palladium complex are discussed on the basis of the substituent effects on the rate of the cross-coupling reactions.*

The highly selective synthesis of unsymmetrical biaryls has recently become of increasing interest in connection with the development of novel organic materials such as organic semiconductors[1] and liquid crystals[2] which possess polyfunctional bi- and polyaryl units. Conventional methods for preparing biphenyls like the Gomberg-Bachmann, the Pschorr, and the Ullman reactions require rather drastic conditions, so they are rarely suitable for the synthesis of functionalized biphenyls.[3] Recent advances in the cross-coupling reactions of arylmetals with aryl halides or triflates using group 10 transition metal catalysts has opened a new route to unsymmetrical biphenyls.[4] A number of aryl metals are known to undergo reactions of this kind; however, the strong nucleophilicity of the metal reagents leads to destruction of reactive functional groups on substrates and the difficult accessibility to the reagents from industrially available precursors often severely limits the applicability of the method.

In a preliminary report,[5a] we have shown that the cross-coupling reaction of aryl(fluoro)silanes with aryl iodides is promoted by $(\eta^3\text{-}C_3H_5PdCl)_2$ catalyst and KF (spray dried) in *N*,*N*-dimethylformamide (DMF), affording the corresponding biaryls in good yields. This reaction tolerates a variety of reactive functional groups, thus offering a reliable method for synthesizing functionalized unsymmetrical biphenyls.

We report herein the scope and the limitations of the cross-coupling reaction of aryl(halo)silanes (halogen = F, Cl), emphasizing the application to the synthesis of liquid crystals and disclose mechanistic aspects of the transmetalation of an aryl(fluoro)silicate intermediate with an arylpalladium complex.

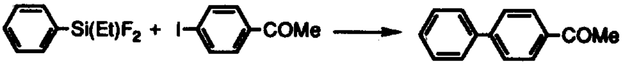
$$\mathrm{Ar{-}Si(halo)}_m\mathrm{R}_{3\text{-}m} + \mathrm{X{-}Ar'} \xrightarrow{\text{Pd cat / KF}} \mathrm{Ar{-}Ar'} \qquad (1)$$

$$\text{halo} = \mathrm{Cl, F};\ \ \mathrm{R} = \mathrm{Me, Et}, n\text{-}\mathrm{Pr, Ar};\ \ m = 1, 2;\ \ \mathrm{X} = \mathrm{Br, I}$$

RESULTS AND DISCUSSION

Cross-Coupling of Aryl(fluoro)silanes with Aryl Iodides. Aryl(fluoro)silanes are prepared in moderate yields (50-60%) by fluorination of the corresponding aryl(chloro)silanes with antimony trifluoride[6] or copper fluoride. In order to estimate the catalytic activity of various palladium complexes and the effect of solvents, a series of reactions were carried out with $PhSi(Et)F_2$ and 4-iodoacetophenone under the various reaction conditions (Table 1).

Table 1. Cross-Coupling of (Ethyl)(difluoro)(phenyl)silane with 4-Iodoacetophenone[a]



entry	catalyst	solvent	reaction time	yield (%)[b]
1	$(\eta^3\text{-}C_3H_5PdCl)_2$[e]	DMF	12 h	71
2	$(\eta^3\text{-}C_3H_5PdCl)_2$[f]	DMF	72 h	38
3[c]	$(\eta^3\text{-}C_3H_5PdCl)_2$[e]	DMF	24 h	30
4[d]	$(\eta^3\text{-}C_3H_5PdCl)_2$[e]	DMF	12 h	94
5	$(\eta^3\text{-}C_3H_5PdCl)_2$[e]	acetone[h]	72 h	41
6	$(\eta^3\text{-}C_3H_5PdCl)_2$[e]	THF[h]	5 h	0
7	$(\eta^3\text{-}C_3H_5PdCl)_2$[e]	dioxane[h]	5 h	0
8	$(\eta^3\text{-}C_3H_5PdCl)_2$[e]	Et_2O[h]	5 h	0
9	$Pd(PPh_3)_4$[g]	DMF	10 h	0
10	$PdCl_2(PPh_3)_2$[g]	DMF	10 h	0
11	$Pd(dba)_2$[g]	DMF	10 h	0
12	$Pd(OAc)_2/P(o\text{-}tol)$[g]	DMF	72 h	58

[a] Unless otherwise noted, reactions were carried out with 4-iodoacetophenone (0.30 mmol) and (difluoro)(ethyl)(phenyl)silane (0.30 mmol) in the presence of a palladium catalyst and KF (0.60 mmol) at 100 °C in 1.5 mL of solvent. [b] Yields were determined by GLC. [c] 4-Bromoacetophenone was used as a substrate. The aryl bromide (49 %) was recovered unchanged. [d] TBAF (0.60 mmol) was used as the fluoride salt. [e] 5.0 mol % of catalyst was used. [f] Catalyst (1.0 mol %) was used. The aryl bromide (58 %) was recovered unchanged. [g] Catalyst (10 mol %) was used. [h] Reaction was carried out in a sealed tube.

The cross-coupling reaction proceeded smoothly in the presence of 5.0 mol % of $(\eta^3\text{-}C_3H_5PdCl)_2$ catalyst and a two fold stoichiometric excess of KF in DMF at 100 °C (entry 1). The reaction was completed within 12 h, giving the cross-coupled product, 4-phenylacetophenone in 71% yield. Attempt to carry out the reaction in the presence of a smaller catalytic amount of palladium catalyst (e.g. 1.0 mol %) resulted in low conversion of the starting material (entry 2). Use of commercially available 4-bromoacetophenone as the halide coupling partner under the same conditions gave the coupled product in low yield, and the halide remained unchanged (entry 3).

Commercially available $n\text{-}Bu_4N^+F^-$ (TBAF) effected the coupling reaction with the highest yield of the coupled product (entry 4), but this could be replaced by inexpensive KF. In contrast, the use of $[(Et_2N)_3S]^+[Me_3SiF_2]^-$ (TASF)[7] as the fluoride salt was totally ineffective.

Palladium complexes such as $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, and $Pd(dba)_2$ did not catalyze at all (entries 9-11). The combination of $Pd(OAc)_2/P(o\text{-tol})_3$ was found to be less effective, since longer reaction times were required even in the presence of 10 mol % of this catalyst (entry 12).

A brief survey of the solvents effect on the reaction (entries 1 and 5-8) revealed that DMF is the solvent of choice (entry 1). Acetone was found to be less effective, causing precipitation of the palladium catalyst prior to completion of the reaction (entry 5). No reaction took place in tetrahydrofuran (THF), diethyl ether, or in dioxane, though these are commonly used solvent for the transition metal catalyzed cross-coupling reaction (entries 6-8).

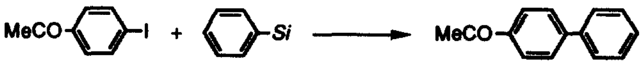
The structure of the aryl(fluoro)silanes was found to decisively effect the efficacy of the cross-coupling reaction in terms of reaction time, the amount of catalyst required for complete substrate conversion, and the yield of coupled product. Various types of phenylsilanes were allowed to react with 4-iodoacetophenone under the standard conditions in order to study the influence of structural variation of the phenylsilane on the cross-coupling reaction (Table 2). The presence of fluorine atoms on the silyl group of the arylsilane was found to be essential for a smooth cross coupling reaction.[8] Thus, phenyl(fluoro)silanes such as $PhSi(Et)F_2$, $PhSi(n\text{-}Pr)F_2$, Ph_3SiF, and Ph_2SiF_2 afforded coupled products in good yields (entries 1-4), whereas tetraorganosilanes such as $PhSiMe_3$ and Ph_4Si failed to give appreciable amounts of the coupled product. Rather, biphenyls arising from the homo-coupling reaction of phenylsilanes were obtained (entries 8-9). However, $PhSiF_3$ failed to give rise to any coupled product (entry 5), and $PhSi(Me)_2F$ gave the low yield of the coupled product (entry 6). When $PhSi(Me)F_2$ was used, competitive methyl coupling reaction with 4-iodoacetophenone took place, furnishing a considerable amount of 4-methylacetophenone along with 4-phenylacetophenone (entry 7).[9]

Our optimum reaction conditions, i.e. 5.0 mol % of $(\eta^2\text{-}C_3H_5PdCl)_2$, 2 equiv. of KF, were applied to the cross coupling reaction of various aryl(difluoro)silanes with aryl iodides. The results summarized in Table 3 show that a range of reactive functional groups on the aryl iodides such as ester (entries 5,9,and 11), ketone (entry 10), aldehyde (entry 12), cyano (entry 6), and hydroxyl (entries 4 and 8) can tolerate the reaction conditions.

The presence of polar substituents on the aryl iodides did not influence the rate of cross coupling. Therefore, the reaction can be successfully applied to aryl iodides possessing not only an electron-withdrawing substituent but also an electron-donating substituent. In contrast, the presence of strong electron-withdrawing substituents such as CF_3 ($\sigma_P = +0.54$) on the aryl(fluoro)silane considerably slowed down the reaction rate, resulting in low yields of the coupled product. For example, 3-iodobenzylalcohol reacted with (4-Me-

$C_6H_4)Si(Et)F_2$ in 86% yield (entry 4), but, (4-CF_3-C_6H_4)$Si(Et)F_2$ gave the coupled product in 64% yield even after extended reaction times (entry 8).

Table 2. Palladium-Catalyzed Cross-Coupling of Various Phenyl(fluoro)silanes with 4-Iodobenzene[a]



entry	Ph—*Si*	reaction time	yield (%)[b]
1	Ph—Si(Et)F_2	12 h	71
2	Ph—Si(*n*-Pr)F_2	12 h	87
3	Ph_3SiF	0.5 h	98
4	Ph_2SiF_2	48 h	74
5	Ph—SiF_3	10 h	0
6	Ph—Si(Me)$_2$F	24 h	15
7	Ph—Si(Me)F_2	12 h	68[c]
8	Ph—$SiMe_3$	24 h	12[d]
9	Ph_4Si	24 h	10[d]

[a] Reactions were carried out with phenyl(fluoro)silane (0.30 mmol) and 4-iodoacetophenone (0.30 mmol) in the presence of (η^3-$C_3H_5PdCl)_2$ (2.5 mol %) and KF (0.6 mmol) in DMF at 100 °C. [b] Yields were determined by GLC. [c] 4-Methylacetophenone was obtained in 14 % yield. [d] Fair amount of biphenyl was obtained.

Table 3. Palladium-Catalyzed Cross-Coupling of Aryl(fluoro)silanes with Aryl Iodides[a]

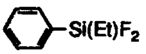
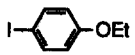
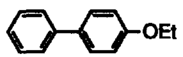
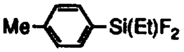
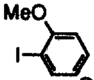
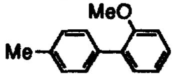
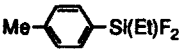
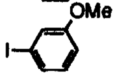
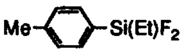
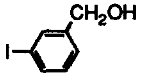
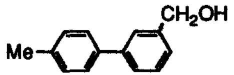
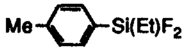
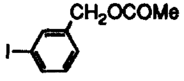
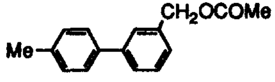
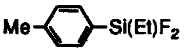
entry	aryl silane	aryl iodide	reaction conditions	product	yield(%)[b]
1			70 °C 10 h		81
2			80 °C 6 h		45
3			80 °C 9 h		83
4			100 °C 15 h		86
5			100 °C 49 h		89
6			100 °C 21 h		67

Table 3. (*continued*)

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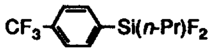
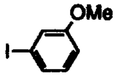
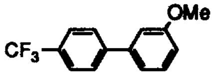
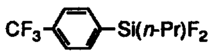
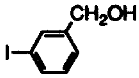
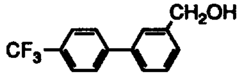
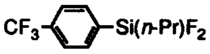
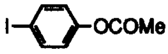
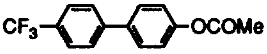
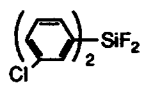
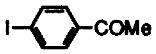
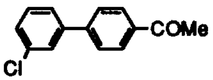
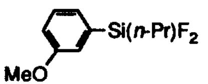
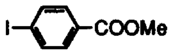
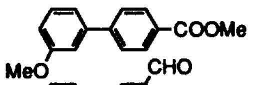
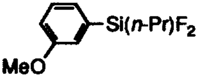
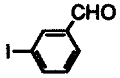
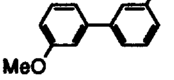
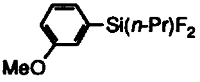
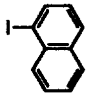
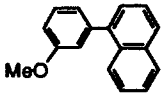
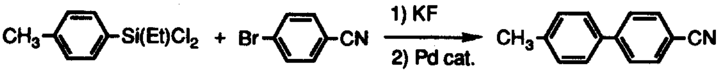
7			80 °C 28 h		52
8			100 °C 19 h		64
9			100 °C 13 h		47
10			70 °C 43 h		74
11			70 °C 15 h		76
12			100 °C 15 h		83
13			100 °C 15 h		94

[a]Coupling reactions were run on a 0.50-5.0 mmol scale with 5.0 mol % of $(\eta^3\text{-}C_3H_5PdCl)_2$ and 2 equiv of KF in DMF. [b]Isolated yields.

Cross-Coupling of Aryl(chloro)silanes with Aryl Halides. In view of the the fluorination of aryl(chloro)silanes with hazardous heavy metal fluorides, *direct* cross-coupling reaction of the parent aryl(chloro)silanes with aryl halides would be desirable. However, the reaction conditions for aryl(fluoro)silanes could not be applied to the coupling reaction of aryl(chloro)silanes with aryl bromides. For example, under the same conditions, commercially available $(4\text{-Me-}C_6H_4)Si(Me)Cl_2$ failed to couple with 4-bromobenzonitrile, and starting material was recovered unchanged.

We have found that aryl(chloro)silanes, *pretreated with KF*, smoothly undergo a palladium catalyzed cross-coupling reaction with aryl bromides to afford unsymmetrical biaryls in moderate to good yields. To optimize the reaction conditions, different combinations of catalysts, ligands, and solvents were tested for the cross-coupling reaction of $(4\text{-Me-}C_6H_4)Si(Me)Cl_2$ with 4-bromobenzonitrile (Table 4). A solution of $(4\text{-Me-}C_6H_4)Si(Me)Cl_2$ and 4-bromobenzonitrile in a solvent shown in Table 4 was treated with KF at 60 °C for 3 h. A palladium catalyst and a ligand were then added to the reaction mixture, and the resulting mixture was stirred at 120 °C for 20 h. The highest yield of the coupled product, 4-cyano-4'-methylbiphenyl (70%), was attained by the use of $Pd(OAc)_2$ (0.5 mol %) and triphenylphosphine (0.5 mol %) in DMF (entry 1). Increasing the amount of $Pd(OAc)_2$ and triphenylphosphine from 0.5 mol % to 5.0 mol % led to competitive homo-coupling reaction of 4-bromobenzonitrile which yielded a considerable amount of 4,4'-dicyanobiphenyl along with the desired cross-coupled product (entry 2). Attempts to carry out the reactions at lower temperatures (60-100 °C) using the same catalyst resulted in incomplete conversion of the starting materials (entry 3).

Table 4. Cross-Coupling of (Dichloro)(ethyl)(4-methylphenyl)silane with 4-Bromobenzonitrile[a]



entry	catalyst	ligand	solvent	yield (%)[b]
1	$Pd(OAc)_2$	PPh_3	DMF	70
2[c]	$Pd(OAc)_2$	PPh_3	DMF	62
3	$Pd(OAc)_2$	PPh_3	DMF[d]	37
4	$Pd(OAc)_2$	PPh_3	acetone[e]	40
5	$Pd(OAc)_2$	PPh_3	THF[e]	0
6	$Pd(OAc)_2$	PPh_3	dioxane[e]	0
7	$Pd(OAc)_2$	PPh_3	Et_2O[e]	0
8	$Pd(dba)_2$	$AsPh_3$	DMF	20 (55)[g]
9	$Pd(OAc)_2$	DPPB[f]	DMF	12
10	$(\eta^3\text{-}C_3H_5PdCl)_2$	—	DMF	0
11	$Pd(PPh_3)_4$	—	DMF	0
12	$PdCl_2(PPh_3)_2$	—	DMF	0
13	$Pd(OAc)_2$	$P(2\text{-Furyl})_3$	DMF	0
14	$Pd(OAc)_2$	$P(OEt)_3$	DMF	0

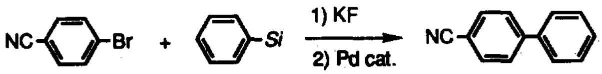
[a] Unless otherwise noted, (dichloro)(ethyl)(4-methylphenyl)silane (0.30 mmol) dissolved in the solvent (1.5 mL) was treated with KF (1.4 mmol) and heated at 60 °C for 3 h. To this mixture a palladium catalyst (0.5 mol %) and a phosphine ligand (0.5 mo l %) were added, and the resulting reaction mixture was stirred at120 °C for 20 h. [b] Isolated yields. [c] Catalyst (5.0 mol %) was used. 4,4'-Dicyanobiphenyl (29%) was obtained. [d] Reaction was carried out at 60-100 °C. The aryl bromide (41%) was recovered. [e] Reaction was carried out in a sealed tube. [f] 1,4-Bis(diphenylphosphino)butane. [g] Reaction time was 72 h.

The combination of $Pd_2(dba)_3(CHCl_3)/AsPh_3$ or $Pd(OAc)_2$ / 1,4-bis(diphenylphosphino)butane (dppb) in DMF were less effective (entries 8 and 9). The palladium complexes such as $(\eta^3\text{-}C_3H_5PdCl)_2$, $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $Pd(OAc)_2/P(2\text{-Furyl})_3$, and $Pd(OAc)_2/P(OEt)_3$ failed to lead to any coupling at all (entries 10-14).

A series of reactions catalyzed by $Pd(OAc)_2$ / triphenylphosphine were conducted in various solvents to examine the solvent effect on the cross-coupling reaction (entries 1 and 4-7). The best result was obtained from the reaction in DMF (entry 1). Reactions in THF, diethyl ether or dioxane gave the coupled product in the low yields (entries 4-7).

The structure of aryl(chloro)silanes also strongly affects the efficiency of the coupling reaction. In order to examine the effect of substituents on the silicon, various types of phenyl(chloro)silanes were allowed to react with 4-bromobenzonitrile under the standard conditions, i.e. 0.50 mol % $Pd(OAc)_2$ and triphenylphosphine, (Table 5). The bulkiness of the alkyl substituent was found to strongly influence the reactivity of the (alkyl)(chloro)(phenyl)silanes. For example, a two fold stoichiometric excess of $PhSi(Me)Cl_2$ was required for complete conversion of 4-bromobenzonitrile (entries 1 and 2), whereas equimolar amount of PhSi(Et)Cl$_2$ sufficed for reaction completion (entry 3). Thus, an ethyl group on the silicon appears to promote the phenyl group transfer from the silicon to the palladium much more effectively than methyl group, probably due to steric release. Commercially available Ph$_2$SiCl$_2$ gave the coupled product in the highest yield (89%) (entry 4). In contrast, PhSi(Me)$_2$Cl gave a rather low yield of the coupled product (entry 5). PhSiCl$_3$ failed to give rise to the product in detectable amount (entry 6).

Table 5. Palladium-Catalyzed Cross Coupling of Various Phenyl(chloro)silanes with 4-Bromobenzonitrile[a]



entry	Ph—*Si*	yield (%)
1	Ph—Si(Me)Cl$_2$	51[b]
2	Ph—Si(Me)Cl$_2$[c]	93
3	Ph—Si(Et)Cl$_2$	70
4	Ph$_2$SiCl$_2$	89
5	Ph—Si(Me)$_2$Cl	37
6	Ph—SiCl$_3$	0

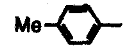
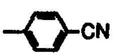
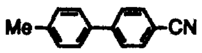
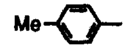
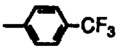
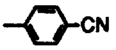
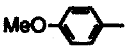
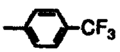
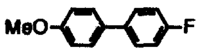
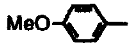
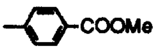
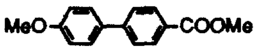
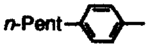
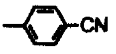
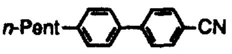
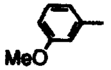
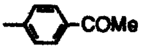
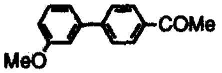
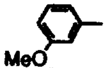
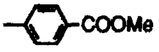
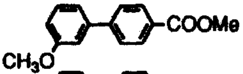
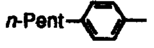
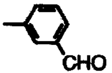
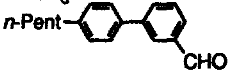
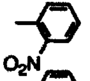
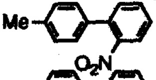
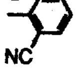
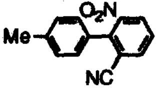
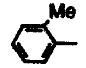
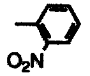
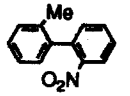
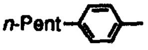
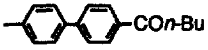
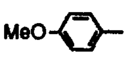
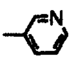
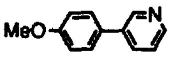
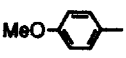
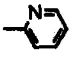
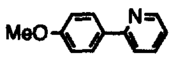
[a] Unless otherwise noted, the reactions were carried out in a way similar to entry 1 of Table 4. [b] 4-Bromobenzonitrile (35%) was recovered unchanged. [c] The silane (0.60 mmol) was used.

Reaction Scope of the Cross-Coupling of Aryl(chloro)silanes. The cross-coupling reactions of aryl bromides bearing various functional groups with Ar-Si(Et)Cl$_2$, pretreated with KF, proceed smoothly at 120 °C in DMF in the presence of Pd(OAc)$_2$ (0.5 mol %) and triphenylphosphine (0.5 mol %). These reactions are much more practical as compared with the cross-coupling reaction of aryl(fluoro)silanes which requires at least 5 mol % of (η^3-C$_3$H$_5$PdCl)$_2$. The results summarized in Table 6 clearly show that aryl-aryl coupling based on aryl(chloro)silanes is a reliable and facile methods for preparing highly functionalized biaryls which are not easily accessible by classical approaches.[3] The synthesis of 4,4'-disubstituted biphenyls for liquid crystals demonstrates the versatility of this method (entries 1-7).[10] Although analogous transition metal catalyzed cross-coupling reactions of the aryl metals of boran, zinc, and tin may potentially be applicable to liquid crystal synthesis,[4] our strategy, based on aryl(chloro)silanes, offers distinct advantages over other cross-coupling methods in view of the availability of various types of aryl(chloro)silanes from industrial sources.[11] In some cases, aryl iodides as the coupling partner gave better results than aryl bromides (entries 2 and 9).

Noteworthy is that the reaction provides a general route to 3,4'-, 2,4'-, and even sterically crowded 2,2'-disubstituted biphenyls as well as 4,4'-disubstituted ones (entries 8-13). For example, (2-Me-C$_6$H$_4$)Si(Et)Cl$_2$ smoothly coupled with 2-bromo-1-nitrobenzene to give 2-methyl-2'-nitrobiphenyl in 88% yield (entry 13). These results apparently show that steric bulkiness of both coupling partners has little effect on the reaction.[12]

Table 6. Palladium-Catalyzed Cross-Coupling of Aryl(dichloro)(ethyl)silanes with Aryl Bromides[a]

$$Ar{-}Si(Et)Cl_2 \quad + \quad Br{-}Ar' \longrightarrow Ar{-}Ar'$$

entry	Ar	Ar'	Ar—Ar'	yield(%)
1				70
2				41 (91)[b]
3				67
4				62
5				91
6				64
7				73
8				70
9				48 (82)[b]
10				54
11				92
12[c]				83
13				88
14				86
15				69
16[d]				23

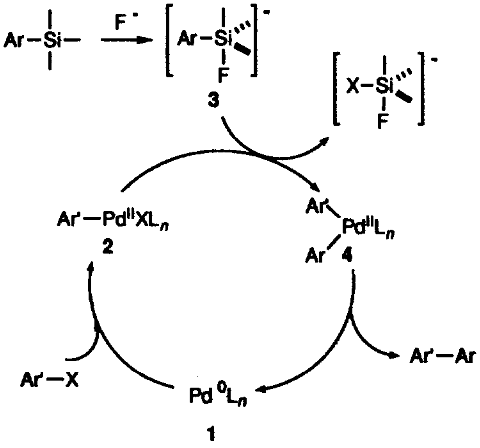
[a] Coupling reactions were run on a 0.50-5.0 mmol scale with $Pd(OAc)_2$ (0.5 mol %) / $P(o\text{-}Tol)_3$ (0.5 mol %) and 2 equiv of KF in DMF at 120 °C. [b] Yields in parentheses are obtained from the reactions of corresponding aryl iodides. [c] Reaction was carried out on 50 mmol scale. [d] As a by-product,1,1'-bipyridyl was obtained in 63%.

Synthesis of *p*-terphenyl was also achieved by the cross-coupling reaction of aryl(chloro)(ethyl)silane with 4-bromobiphenyl (entry 14).[13] A practical route to functionalized *p*-terphenyls is particularly important for their extensive use as liquid crystals.[2]

We next studied the extension of this reaction to the synthesis of heteroaromatics. Under the standard conditions, (4-MeO-C_6H_4)Si(Et)Cl_2 smoothly coupled with 3-bromopyridine, affording 3-(4-methoxyphenyl)pyridine in a satisfactory 69% yield (entry 15). However, reaction with 2-bromopyridine furnished a substantial amount of 2, 2'-bipyridyl as the result of homo-coupling of 2-bromopyridine, along with the desired cross-coupled product (entry 16).

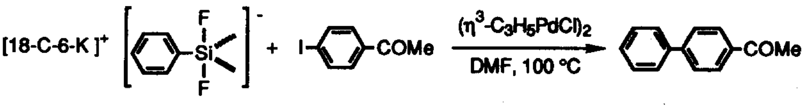
Mechanistic Studies. A mechanism for the palladium catalyzed cross-coupling reaction of aryl(halo)silanes with aryl halides most likely involves (1) oxidative addition of the aryl halide to a palladium(0) complexe **1** to generate an arylpalladium(II) complex **2**, (2) transmetalation of **2** with an anionic pentacoordinate aryl(fluoro)silicate **3** which is formed by nucleophilic attack of fluoride ion on the aryl(halo)silane, yielding a corresponding bis(aryl)palladium(II) complex **4**, and (3) reductive elimination of **4** to give the coupled product and regenerate **1** (Scheme 1).

Scheme 1.



With the aim of providing the some evidence for the participation of a pentacoordinate aryl(fluoro)silicate **3** as an active species, the reactivity of [18-crown-6-K]$^+$[Ph$_n$SiF$_{5-n}$]$^-$ (n = 1, 2, 3) in the aryl-aryl coupling reaction were compared with that of the (fluoro)(phenyl)silanes / KF system. A series of pentacoordinate aryl(fluoro)silicates were prepared from phenyl(chloro)silanes, KF, and 18-crown-6 acoding to the literature procedure.[14] These silicates coupled with 4-iodoacetophenone in the presence of (η^3-$C_3H_5PdCl)_2$ (5.0 mol %) in DMF at 100 °C to yield 4-acetylbiphenyls. The results summarized in Table 7 shows that the reactivity of the silicates critically depends on the number of fluorine atoms on the silicon.

Table 7. Palladium Catalyzed Cross-Coupling of Phenyl(fluoro)silicates with 4-Iodoacetophenone[a]



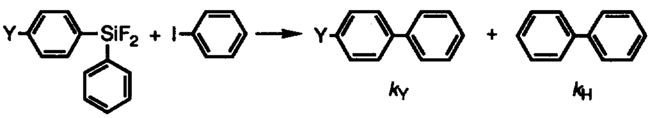
silicate	reaction time	yield of coupled product
$[PhSiF_4]^-$	18 h	no reaction
$[Ph_2SiF_3]^-$	48 h	52
$[Ph_3SiF_2]^-$	5 h	96

[a]Reactions were carried out with a silicate (0.30 mmol) and 4-iodoacetophenone (0.30 mmol) in the presence of $(\eta^3\text{-}C_3H_5PdCl)_2$ (5.0 mol %) in DMF at 100 °C.

The reactivity of the pentacoordinate (fluoro)(phenyl)silicates decreased in the order $[Ph_3SiF_2]^- > [Ph_2SiF_3]^- >> [PhSiF_4]^-$. This reactivity order is apparently in accord with that of (fluoro)(phenyl)silanes in the cross-coupling with 4-iodoacetophenone, i.e. $Ph_3SiF > Ph_2SiF_2 >> PhSiF_3$ (see Table 2, entries 3-5). Comparison of these results strongly suggests that the pentacoordinate silicate $[Ph_nSiF_{5-n}]^-$ is an active species in the cross coupling reaction using the KF/ Ph_nSiF_{4-n} system.

The transmetalation of main group organometallics with transition metal complexes is one of the key reactions involved in many catalytic processes. However, mechanistic aspects of this process still remain ambiguous.[15] A series of intramolecularly competitive reactions of unsymmetrical (diaryl)(difluoro)silanes with phenyl iodide were carried out in order to study substituent effects on the transmetalation of an aryl(fluoro)silicate with an arylpalladium(II) complex (Table 8).

Table 8. Relative Initial Rates of the Palladium Catalyzed Cross-Coupling Reaction of Unsymmetrically Substituted Diaryl(difluoro)silanes with Iodobenzene



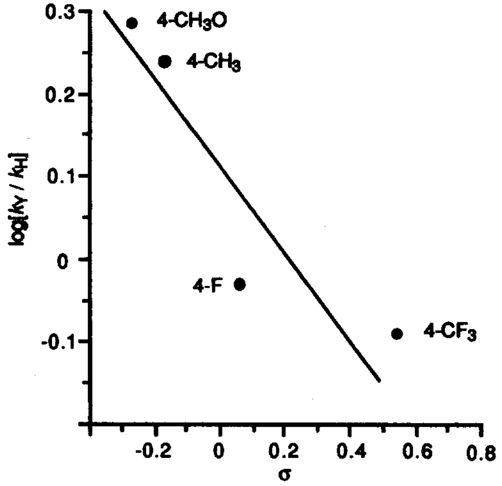
Y = MeO, Me, H, F, CF_3

	rel. rate	
substituent	k_Y / k_H	$\log[k_Y / k_H]$
4-OMe	1.92	0.28
4-Me	1.71	0.23
H	1.00	0.00
4-F	0.93	-0.031
$4\text{-}CF_3$	0.80	-0.097

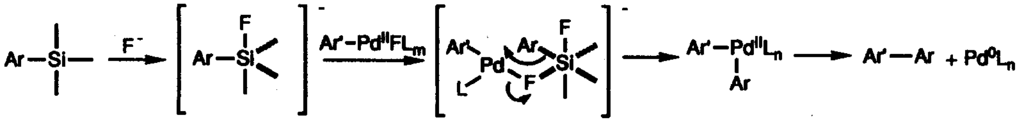
As a product, a mixture of 4-substituted biphenyls and biphenyls were formed. The product ratio was found to be decisively influenced by the electronic nature of the 4-substituent.[16] Thus, an electron-donating group such as methoxy or methyl groups accelerated the reaction, whereas an electron-withdrawing group such as a fluorine or trifluoromethyl group retarded the reaction. The initial rate (k_Y and k_H) of the cross-coupling reactions using an excess amount of phenyl iodide was calculated for each substituent Y based on the relative rate of the formation of the two products.

The relative initial rate obtained for each substituent is plotted against the Hammett σ value (Figure 1). Negative ρ value ($\rho = -1.5$) clearly indicates the electrophilic character of the transmetalation. Thus, it can be concluded that the transfer of the aryl group from silicon to palladium is initiated by electrophilic attack of the arylpalladium(II) complex to the aryl-silicon bond (S_E reaction). The presence of an electron-donating substituent enhances the nucleophilicity of the aryl-silicon bond, thus promoting the electrophilic attack of the arylpalladium(II) complex (Scheme 2). This process is considered to proceed via a Si-Pd binuclear intermediate formed by a fluoride bridge.[5b,15]

Figure 1. Hammett plot of the reaction of unsymmetrically substituted diaryl(difluoro)silanes with iodobenzene



Scheme 2.



CONCLUSIONS

Aryl(fluoro)silanes and aryl(chloro)silanes have been shown to be excellent reagents for use in palladium catalyzed cross-coupling reactions with aryl halides. The reaction is tolerant of a wide variety of functional groups, therefore providing a general and reliable route to highly functionalized biphenyls and *p*-terphenyl. In view of the recent development of material science, this aryl-aryl coupling reaction based on industrially accessible aryl(chloro)silanes is an extremely practical and efficient method for synthesizing the biaryl units of organic materials such as liquid crystals and semiconductors.

For the smooth coupling reaction of aryl(chloro)silanes, it is essential to treat the silanes with KF *prior* to addition of the palladium catalyst in order to generate an anionic pentacoordinate aryl(fluoro)silicate which is the active intermediate undergoing transmetalation with the arylpalladium(II) complex. On the basis of observed substituent effect on the reaction rate, a mechanism for the transmetalation between the aryl(fluoro)silicates and the arylpalladium(II) complex has been proposed where aryl transfer from silicon to palladium proceeds via the S_E reaction of the arylpalladium(II) complex with the pentacoordinate (aryl)(fluoro)silicate.

EXPERIMENTAL

General. All melting points were uncorrected. The ^{1}H NMR spectra were recorded on a Brucker AC-200P (200 MHz) or a Brucker AM-400 (400 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Infrared spectra were obtained on a JASCO A-202 spectrometer. Elemental analyses were carried out on a Perkin Elmer Model 240. Mass spectra were recorded on a Hitachi M-80 (low-resolution mass spectra) or a Hitachi M-80BS (high-resolution mass spectra). Gas chromatographic analyses were performed on a Shimadzu GC-14A equipped with a 0.25 mm x 50 m, OV-1 capillary column and a flame ionization detector. Tetrahydrofuran (THF), dioxane and benzene were freshly distilled from sodium/benzophenone. *N,N*-dimethylformamide (DMF) was distilled at reduced pressure from calcium hydride. Potassium fluoride (spray dried) was purchased from Wako Chemical Co. and used without further purification.

Aryl Halides. 3-Iodobenzylalcohol, 2-iodoanisole, 3-iodoanisole, 4-iodoanisole, 4-iodoacetophenone, and 1-iodonaphthalene were obtained from the Aldrich Chemical Co. (3-Iodophenyl)methyl acetate and 4-iodophenyl acetate were prepared by the reaction of the corresponding alcohols with acetyl chloride in the presence of triethylamine in dichloromethane. 4-Iodobenzonitrile was synthesized from 4-iodoaniline according to the literature procedure.[17] 3-Iodobenzaldehyde was prepared by oxidation of 3-iodobenzylalcohol using pyridinium chlorochromate in dichloromethane. Methyl 4-iodobenzoate was prepared by the esterification of 4-iodobenzoic acid with diazomethane in diethyl ether. All aryl bromides used in this work, except 4-bromo-4'-pentanoylbiphenyl, were commercially available. 4-Bromo-4'-pentanoylbiphenyl was synthesized in 58% yield by means of the Friedel-Crafts reaction of pentanoyl chloride with 4-bromobiphenyl according to usual procedures[18] as a colorless solid: mp 101-102 °C; IR (KBr) 2955, 1676, 1604, 1387, 1206, 795 cm^{-1}; ^{1}H NMR (200 MHz): δ 0.97 (t, J = 7.4 Hz, 3H), 1.43 (sextet, J = 7.4 Hz, 2H), 1.75 (quintet, J = 7.4 Hz, 2H), 2.99 (t, J = 7.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.60 (t, J = 8.4 Hz, 4H), 8.03 (d, J = 8.4 Hz, 2H). Anal. Calcd for $C_{17}H_{17}BrO$: C, 64.37; H, 5.40. Found: C, 64.31; H, 5.42.

Arylsilanes. (Dichloro)(phenyl)(methyl)silane, (dichloro)(phenyl)(ethyl)silane, (dichloro)(diphenyl)silane, (chloro)(dimethyl)(phenyl)silane (fluoro)(triphenyl)silane, (difluoro)(diphenyl)silane, (trimethyl)(phenyl)silane, tetraphenylsilane, and (trichloro)(phenyl)silane were obtained from Shin-etsu Chemical Co. and used without further purification. The following compounds were prepared by the literature procedures: (ethyl)(difluoro)(phenyl)silane,[6] (ethyl)(difluoro)(4-methylphenyl)silane,[6] (difluoro)[4-(trifluoromethyl)phenyl](*n*-propyl)silane,[6] (difluoro)(3-methoxylphenyl)(*n*-propyl)silane, (dichloro)(ethyl)(4-methylphenyl)silane,[6] (difluoro)(4-methylphenyl)(phenyl)silane,[19] di(3-chlorophenyl)(difluoro)silane,[19] and (difluoro)(4-fluorophenyl)(phenyl)silane.[19]

(Dichloro)(ethyl)(4-methoxyphenyl)silane. A solution of (4-methoxyphenyl)magnesium bromide prepared from 4-bromoanisole (5.6 g, 30 mmol) and magnesium (0.88 g, 36 mmol) in THF (15 mL) was added dropwise over 20 min to a solution of (trichloro)(ethyl)silane (4.91 g, 30 mmol) in THF (35 mL) at 0 °C. After the solution was stirred at the room temperature for 12 h, the bulk of the solvent was removed under reduced pressure and dry hexane (50 mL) was then added. The resulting slurry was filtered and the filtrate was concentrated under reduced pressure (1 mm for 2 h) to give (dichloro)(ethyl)(4-methoxyphenyl)silane as a brown oil which was pure enough for the use in cross-coupling reaction without further purification (6.9 g, 29 mmol, 97%): bp 109 °C (1.7 mm); IR (neat) 3060, 2960, 1597, 1286, 1119, 821, 698 cm^{-1}; ^{1}H NMR (90 MHz): δ 0.95-1.45 (m, 5H), 3.84 (s, 3H), 6.97 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H); HRMS for $C_9H_{12}OSiCl_2$ calcd 234.0033, found 234.0030.

(Dichloro)(ethyl)(3-methoxyphenyl)silane was prepared in 96% yield by the same procedure. The crude product was pure enough for in the cross-coupling reaction: bp (bulb-to-bulb) 110 °C (2.0 mm); IR (neat) 3030, 2960, 1597, 1289, 1252, 1041, 1051, 784, 702 cm^{-1}; ^{1}H NMR (400 MHz): δ 1.14 (t, J = 7.6 Hz, 3H), 1.33 (q, J = 7.6 Hz, 2H), 3.87 (s, 3H), 7.04 (ddd, J = 7.8, 2.7, 1.0 Hz, 1H), 7.24 (dd, J = 2.7, 0.8 Hz, 1H), 7.28 (ddd, J = 7.8, 1.0, 0.8 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H); HRMS for $C_9H_{12}OSiCl_2$ calcd 234.0033, found 234.0020.

(Dichloro)(ethyl)[4-(pentyl)phenyl]silane was prepared in 96% yield by the same procedure. This can be used in the cross-coupling reaction without distillation: bp 123-126 °C (1.0 mm); IR (neat) 3030, 2980, 1605, 1240, 1118, 801, 695 cm^{-1}; ^{1}H NMR (90 MHz): δ 0.89 (t, J = 5.8 Hz, 3H), 1.05-1.90 (m, 11H), 2.64 (t, J = 7.3 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H); ; HRMS for $C_{13}H_{20}SiCl_2$ calcd 274.0710, found 274.0732.

(Difluoro)(4-methoxyphenyl)(phenyl)silane. To a solution of trichloro(phenyl)silane (21 g, 100 mmol) in THF (30 mL) was added (4-methoxyphenyl)magnesium bromide prepared from 4-bromoanisole (8.4 g, 45 mmol) and magnesium (1.3 g, 54 mmol) in THF (40 mL). After stirring at room temperature for 12 h, the bulk of the solvent was removed under reduced pressure and dry hexane (100 mL) then added. The resulting slurry was filtered and the filtrate was concentrated to give a brown oil which was distilled at 160 °C (1.0 mm) to afford (dichloro)(4-methoxyphenyl)(phenyl)silane as a colorless oil (8.1 g, 29 mmol, 64%): IR (neat) 3060, 2960, 1400, 1260, 845, 790 cm^{-1}; ^{1}H NMR (90 MHz): δ 3.80 (s, 6H), 7.05 (d, J = 8.0 Hz, 2H), 7.35-8.00 (m, 7H). This chlorosilane was converted to the corresponding fluorosilane. A solution of (dichloro)(4-methoxyphenyl)(phenyl)silane (8.1 g, 29 mmol) in ether (20 mL) was added to a suspension of CuF_2 $2H_2O$ (4.1 g, 30 mmol) in ether (20 mL) at 0 °C, and the resulting reaction mixture was stirred at room temperature for 8 h. The mixture was then diluted with pentane (50 ml) and filtered. The filtrate was dried over $MgSO_4$ and concentrated to give (difluoro)(4-methoxyphenyl)(phenyl)silane (3.4 g, 14 mmol, 47%): bp 114 °C (0.25 mm); IR (neat) 3100, 1600, 1286, 920, 860 cm^{-1}; ^{1}H NMR (90 MHz): δ 3.85 (s, 3H), 6.95 (d, J = 9 Hz, 2H), 7.30-7.80 (m, 7H). Anal. Calcd for $C_{13}H_{12}SiF_2$: C, 62.38; H, 4.83. Found: C, 62.22; H, 4.84.

(Difluoro)[(4-trifluoromethyl)phenyl](phenyl)silane was synthesized in 65% yield by the same procedure: bp 62-63 °C (0.05 mm); IR (neat) 3100, 1340, 1170, 1130, 1118, 915, 860, 830, 720, 540 cm^{-1}; ^{1}H NMR (90 MHz): δ 7.44-7.80 (m, 7H), 7.84 (d, J = 8.1 Hz, 2H). Anal. Calcd for $C_{13}H_9SiF_5$: C, 54.16; H, 3.15. Found: C, 54.10; H, 3.22.

Coupled Products. The spectra and the physical properties of the following products were consistent with the reported data: 4-cyano-4'-methylbiphenyl,[20] 4-trifluoromethyl-4'-methylbiphenyl,[21] 4-cyano-4'-methoxybiphenyl,[20] 4-trifluoromethyl-4'-methoxybiphenyl,[22] 4-fluoro-4'-methoxybiphenyl,[23] methyl 4-(4-methoxyphenyl)benzoate,[24] 4-cyano-4'-(1-pentyl)biphenyl,[25] 4-acetyl-3'-methoxybiphenyl,[26] 4-methyl-2'-nitrobiphenyl,[27] 2-cyano-4'-methylbiphenyl,[26] 2-methyl-2'-nitrobiphenyl,[27] 1-methoxy-4-(3-pyridyl)benzene,[28] 1-methoxy-4-(2-pyridyl)benzene,[29] methyl 4-(3-methoxyphenyl)benzoate.[30]

General Procedure for the Cross-coupling Reaction of Aryl(fluoro)silanes with Aryl Iodides. 4-Methyl-3'-(hydroxymethyl)biphenyl (Table 3, entry 4): To a suspension of 350 mg (6.0 mmol) of potassium fluoride (spray dried) in DMF (50 mL) were added 560 mg (3.0 mmol) of (ethyl)(difluoro)(4-methylphenyl)silane, 250 mg (2.0 mmol) of 3-iodobenzyl alcohol, and 37 mg (0.1 mmol, 5 mol %) of $(\eta^3\text{-}C_3H_5PdCl)_2$. The resulting mixture was stirred at 100 °C for 15 h, then cooled to room temperature, poured into saturated aqueous sodium bicarbonate solution, and extracted with diethyl ether (20 mL x 3). The combined ethereal layer was then dried over magnesium sulfate. Removal of the solvent under reduced pressure afforded a crude material, which was purified by silica-gel column chromatography (hexane /

ethyl acetate, 5 : 1) to give 340 mg (1.7 mmol, 86 %) of 3-hydroxymethyl-4'-methylbiphenyl as a colorless solid: mp 73-74 °C; TLC (hexane / ethyl acetate, 5 : 1) R_f 0.12; IR (KBr) 3375, 2925, 1485, 1340, 1185, 1050, 895, 820, 780, 700 cm^{-1}; ^{1}H NMR (90 MHz): δ 1.87 (s, 1H), 2.37 (s, 3H), 4.70 (s, 2H), 7.46-7.60 (m, 8H). Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.75; H, 7.14.

The following compounds were prepared in an analogous fashion:

2-Methoxy-4'-methylbiphenyl (Table 3, entry 2): colorless solid; mp 70-72 °C; TLC (hexane) R_f 0.50; IR (KBr) 2970, 1485, 1450, 1230, 1175, 1105, 1055, 1120, 825, 760 cm^{-1}; ^{1}H NMR (90 MHz): δ 2.40 (s, 3H), 3.84 (s, 3H), 6.90-7.53 (m, 8H). Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.77; H, 7.38.

3-Methoxy-4'-methylbiphenyl (Table 3, entry 3): colorless oil; TLC (hexane) R_f 0.52; IR (neat) 2970, 1600, 1480, 1295, 1220, 1055, 1030, 820, 780 cm^{-1}; ^{1}H NMR (90 MHz): δ 2.40 (s, 3H), 3.85 (s, 3H), 6.80-7.56 (m, 8H). Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.87; H, 7.12.

3-Acetoxymethyl-4'-(methyl)biphenyl (Table 3, entry 5): colorless oil; TLC (hexane / ethyl acetate, 10 : 1) R_f 0.40; IR (neat) 3050, 1750, 1380, 1225, 1025, 820, 790, 700 cm^{-1}; ^{1}H NMR (90 MHz): δ 2.10 (s, 3H), 2.40 (s, 3H), 5.10 (s, 2H), 7.10-7.70 (m, 8H). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.91; H, 6.77.

3-Methoxy-4'-(trifluoromethyl)biphenyl (Table 3, entry 7): colorless oil; TLC (hexane / ethyl acetate, 5 : 1) R_f 0.80; IR (neat) 3040, 2950, 1600, 1325, 1220, 1170, 1110, 840, 780, 695 cm^{-1}; ^{1}H NMR (90 MHz): δ 3.87 (s, 3H), 6.86-7.50 (m, 4H), 7.66 (s, 4H). Anal. Calcd for $C_{14}H_{11}F_3O$: C, 66.67; H, 4.40. Found: C, 66.65; H, 4.53.

3-Hydroxymethyl-4'-(trifluoromethyl)biphenyl (Table 3, entry 8): colorless oil; TLC (hexane / ethyl acetate, 5 : 1) R_f 0.12; IR (neat) 3350, 3050, 1660, 1610, 1320, 1160, 1110, 840, 770, 695 cm^{-1}; ^{1}H NMR (90 MHz): δ 1.78 (s, 1H), 4.76 (s, 2H), 7.20-7.80 (m, 4H), 7.63 (s, 4H). Anal. Calcd for $C_{14}H_{11}F_3O$: C, 66.67; H, 4.40. Found: C, 66.61; H, 4.53.

4-Acetoxy-4'-(trifluoromethyl)biphenyl (Table 3, entry 9): colorless solid; mp 70-72 °C; TLC (hexane / ethyl acetate, 10 : 1) R_f 0.43; IR (KBr) 3070, 1760, 1335, 1220, 1170, 1125, 1080, 840 cm^{-1}; ^{1}H NMR (90 MHz): δ 2.34 (s, 3H), 7.14 (d, J = 8 Hz, 2H), 7.55 (d, J = 8 Hz, 2H), 7.63 (s, 4H). Anal. Calcd for $C_{15}H_{11}F_3O_2$: C, 64.29; H, 3.96. Found: C, 64.25; H, 4.03.

4-Acetyl-3'-chlorobiphenyl (Table 3, entry 10): colorless oil; TLC (hexane / ethyl acetate, 10 : 1) R_f 0.45; IR (neat) 3350, 3060, 1685, 1600, 1265, 955, 785, 590 cm^{-1}; ^{1}H NMR (90 MHz): δ 2.60 (s, 3H), 7.27-7.75 (m, 4H), 7.63 (d, J = 7.5 Hz, 2H), 8.06 (d, J = 7.5 Hz, 2H). Anal. Calcd for $C_{14}H_{11}ClO$: C, 72.89; H, 4.81. Found: C, 72.81; H, 4.91.

Methyl 4-(3-methoxyphenyl)benzoate (Table 3, entry 11): colorless oil; TLC (hexane / ethyl acetate, 10 : 1) R_f 0.41; IR (neat) 2950, 1720, 1600, 1275, 1105, 850, 765, 690 cm^{-1}; ^{1}H NMR (90 MHz): δ 3.85 (s, 3H), 3.96 (s, 3H), 6.90-7.52 (m, 4H), 7.68 (d, J = 8 Hz, 2H), 8.12 (d, J = 8 Hz, 2H). Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83. Found: C, 74.27; H, 5.88.

3-(3-methoxyphenyl)benzaldehyde (Table 3, entry 12): colorless oil; TLC (hexane / ethyl acetate, 10 : 1) R_f 0.51; IR (neat) 2950, 2730, 1695, 1600, 1225, 1160, 780, 690 cm^{-1}; ^{1}H NMR (90 MHz): δ 3.87 (s, 3H), 6.95-8.18 (m, 8H), 10.15 (s, 1H). Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.11; H, 5.58.

1-(3-methoxyphenyl)naphthalene (Table 3, entry 13): colorless oil; TLC (hexane) R_f 0.70; IR (neat) 3050, 2950, 1575, 1460, 1220 1165, 1040, 770, 700 cm^{-1}; ^{1}H NMR (90 MHz): δ 3.87 (s, 3H), 6.83-8.23 (m, 11H). Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.11; H, 6.12.

General Procedure for the Cross-Coupling Reaction of Aryl(chloro)silanes with Aryl Bromides. 4-Fluoro-4'-methoxybiphenyl (Table 6, entry 5): To a suspension of 2.1 g (36 mmol) of potassium fluoride (spray dried) in DMF (7.0 mL) was added 1.7 g (7.2 mmol) of (dichloro)(ethyl)(4-methoxyphenyl)silane and 1.05 g (6.0 mmol) of 4-fluoro-1-bromobenzene at 0 °C under an atmosphere of argon. The resulting reaction mixture was then stirred at 60 °C for 3 h. The mixture was allowed to cool to room temperature, and a solution of 6.7 mg (0.030 mmol, 0.50 mol %) of palladium acetate and 7.8 mg (0.030 mmol, 0.50 mol %) of triphenylphosphine in DMF (7.0 mL) was added. The reaction mixture was heated at 120 °C for 18 h and then cooled to room temperature, poured into a saturated aqueous sodium chloride solution and extracted with ethyl acetate (20 mL x 3). The combined organic extracts were then dried over magnesium sulfate. Removal of the solvent under reduced pressure (1 mm for 1 h) afforded a crude product, which was purified by silica-gel column chromatography (hexane : ethyl acetate = 10 : 1) to give 1.11 g (5.5 mmol, 91 %) of 4-fluoro-4'-methoxybiphenyl: mp 94-96 °C (lit.[21] 90-91 °C); IR (KBr) 3030, 1610, 1495, 1240, 1040, 828, 810 cm^{-1}; ^1H NMR (400 MHz): δ 3.84 (s, 3H), 6.94 (d, J = 8.8 Hz, 2H), 7.09 (t, J = 8.8 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.48 (dd, J = 8.8, 5.3 Hz, 2H).

The following compounds were prepared in an analogous fashion:

3-Formyl-4'-(pentyl)biphenyl (Table 6, entry 10): colorless oil; TLC (hexane / ethyl acetate, 10 : 1) R_f 0.51; IR (neat) 2957, 2930, 1701, 1180, 837, 790 cm^{-1}; ^1H NMR (400 MHz): δ 0.90 (t, J = 6.7 Hz, 3H), 1.32-1.42 (m, 4H), 1.61-1.71 (m, 2H), 2.66 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.59 (t, J = 7.7 Hz, 1H), 7.81-7.88 (m, 2H), 8.09 (t, J = 1.5 Hz, 1H), 10.1 (s, 1H). Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.75; H, 7.79.

4-Pentyl-4"-(1-oxopentyl)-*p*-terphenyl (Table 6 entry 14): colorless crystal; mp 208-210 °C (ethyl acetate); IR (KBr) 3050, 2955, 2930, 1680, 1601, 800, 794 cm^{-1}; ^1H NMR (400 MHz): δ 0.91 (t, J = 6.2 Hz, 3H), 0.97 (t, J = 7.2 Hz, 3H), 1.23 -1.51(m, 6H), 1.60-1.83 (m, 4H), 2.66 (t, J = 8.0 Hz, 2H), 3.01 (t, J = 7.4 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 7.70 (s, 4H), 7.56 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 8.40 (d, J = 8.4 Hz, 2H); MS (EI) *m/z* (%) 384 (M^+, 76), 342 (79), 327(100), 242(44), 228 (15). Anal. Calcd for $C_{28}H_{32}O$: C, 87.45; H, 8.39. Found: C, 87.58; H, 8.27.

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