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CARBONYLATIVE COUPLING REACTION OF ORGANOFLUOROSILANES WITH ORGANIC HALIDES PROMOTED BY FLUORIDE ION AND PALLADIUM CATALYST

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Key Words: *carbonylative coupling; organofluorosilanes; ketone synthesis*

Abstract: *Palladium-catalyzed carbonylative cross coupling reaction of organofluorosilanes with organic halides was achieved in the presence of fluoride ion and an atmospheric pressure of carbon monoxide. Alkenyl- or arylfluorosilanes effectively underwent this reaction with alkenyl or aryl iodides in moderate to good yields. Thus, highly functionalized ketones are readily available without protection of reactive functional group such as aldehyde, ketone, ester, nitrile, and alcohol. For smooth ketone formation, use of organofluorosilanes is essential; tetraorganosilanes like aryl(trimethyl)silanes, upon reaction with aryl iodides, gave aroyl fluorides instead.*

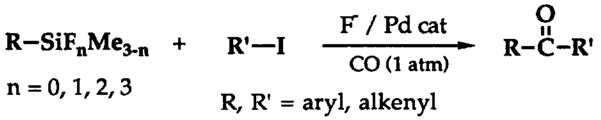
Transition metal catalyzed carbonylative cross coupling reaction of organometallic compounds with electrophiles is one of the most straightforward route to unsymmetrical ketones. Although organometallic reagents of Sn,[1] B,[2] Al,[3] and Hg[4] have been successfully utilized for this type of reaction, conditions requiring high CO pressure and/or limited combinations of an organometal and an electrophile have made this reaction less accessible. For example, no alkenyl metal has been shown to undergo carbonylative coupling with aryl halides to give alkenyl aryl ketones in reasonable yields.[1f]

We have recently reported that cross coupling of organosilicon compounds with organic halides promoted by fluoride ion and a palladium catalyst provides an efficient method for carbon-carbon bond formation (eq 1).[5] The presence of fluoride ion is essential for accelerating the transmetalation step in which a pentacoordinate silicate,[6] formed by reaction of fluoride ion with an organosilane, transfers an organic group to palladium(II) species.[5b] One of striking features of this reaction is that a carbonyl group on either coupling partner tolerates the reaction conditions. This observation prompted us to extend the reaction to ketone synthesis through carbonylative cross coupling reaction. In a preliminary report[7] we have shown that

$$\text{R–SiF}_n\text{Me}_{3\text{-}n} + \text{R'–X} \xrightarrow{\text{F}^- / \text{Pd cat}} \text{R–R'} \qquad (1)$$

$$n = 0, 1, 2, 3 \qquad \begin{array}{l}\text{R = alkyl, allyl, aryl, alkenyl, alkynyl}\\ \text{X = Br, I}\end{array}$$

the desired carbonyl insertion successfully takes place between aryl(alkyl)difluorosilanes and aryl iodides under the influence of a palladium catalyst, fluoride ion, and an atmospheric pressure of carbon monoxide to give diaryl ketones in good yields. We report herein scope and limitations of the carbonylative cross coupling of organosilicon compounds and organic halides (eq 2).



$$\text{R–SiF}_n\text{Me}_{3\text{-}n} + \text{R'–I} \xrightarrow[\text{CO (1 atm)}]{\text{F}^- / \text{Pd cat}} \text{R–}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{–R'} \qquad (2)$$

$$n = 0, 1, 2, 3 \qquad \text{R, R' = aryl, alkenyl}$$

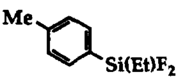
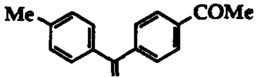
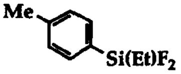
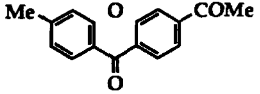
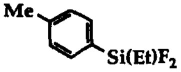
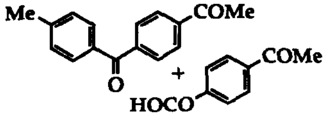
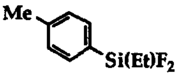
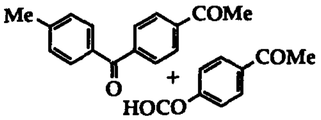
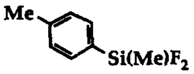
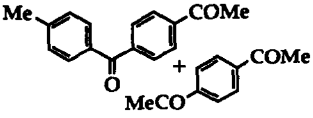
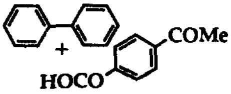
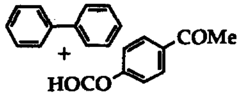
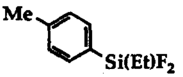
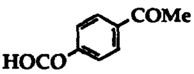
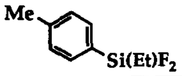
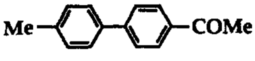
Results and Discussion

Carbonylative Coupling of Arylfluorosilanes and Aryl and Alkenyl Iodides. In order to evaluate the reactivity of arylsilanes capable of the desired carbonylative coupling, a series of reactions using various types of arylsilanes with 1-(4-iodophenyl)ethanone were carried out in the presence of a palladium catalyst and a fluoride salt under an atmosphere of carbon monoxide. The results are summarized in Table I. Since the combination of the $(\eta^3\text{-C}_3\text{H}_5\text{PdCl})_2$ catalyst, KF, and *N, N*-dimethylformamide (DMF) solvent was effective for the direct cross coupling of ArSi(R)F_2 with aryl iodides,[5c] we first applied these conditions to the reaction of (4-acetylphenyl)(ethyl)difluorosilane with 1-(4-iodophenyl)ethanone. As shown in entry 1, carbonylative coupling proceeded sluggishly to afford the expected ketone in moderate yield. Better results were obtained by using *N, N*-dimethyl-2-imidazolidinone (DMI) as the solvent (entry 2). The reaction was complete within 3 h to give 4-acetylphenyl 4-methylphenyl ketone in 91% yield. In contrast, use of a phosphine-based palladium catalyst like $\text{Pd(PPh}_3)_4$ or $\text{PdCl}_2(\text{PPh}_3)_2$ caused carboxylation of the aryl iodide, giving 4-acetylbenzoic acid in fair amounts (entries 3 and 4).

A substituent on silicon also strongly affected the product distribution. The aryl group of ArSi(Et)F_2 reacted in preference to the ethyl group, and the expected diaryl ketone was obtained as a sole product in good yield (entry 2). However, the methyl group of PhSi(Me)F_2 reacted competitively, giving rise to a fair amount of a methyl ketone 1,4-diacetylbenzene (entry 5).

The presence of fluorine on the silyl group is indispensable for a smooth reaction: PhSiMe_3 and Ph_4Si failed to give appreciable amounts of 4-acetylphenyl phenyl ketone, affording instead a mixture of biphenyl and 4-acetylbenzoic acid (entries 6 and 7). The role of fluorine on silicon can be explained in terms of stabilization of an anionic silicate intermediate.

Table I. Pd-Catalyzed Carbonylative Coupling of Arylsilanes with 4-Iodoacetophenone[a]

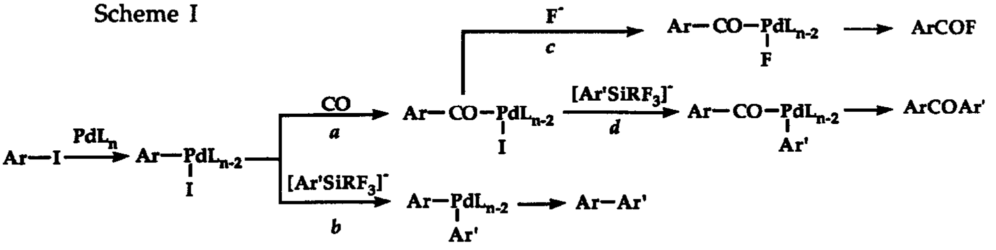
Entry	Arylsilane	Catalyst	Reaction Time (h)	Product(s)	(Yield %)[b]
1[c]		$(\eta^3\text{-}C_3H_5PdCl)_2$	48		(41)
2		$(\eta^3\text{-}C_3H_5PdCl)_2$	3		(91)
3		$PdCl_2(PPh_3)_2$	12		(34) (46)
4		$Pd(PPh_3)_4$	12		(51) (43)
5		$(\eta^3\text{-}C_3H_5PdCl)_2$	12		(72) (20)
6	$PhSiMe_3$	$(\eta^3\text{-}C_3H_5PdCl)_2$	12		(14) (52)
7	Ph_4Si	$(\eta^3\text{-}C_3H_5PdCl)_2$	12		(23) (49)
8	$PhSiF_3$	$(\eta^3\text{-}C_3H_5PdCl)_2$	10	no reaction	
9[d]		$(\eta^3\text{-}C_3H_5PdCl)_2$	12		(64)
10[e]		$(\eta^3\text{-}C_3H_5PdCl)_2$	1		(73)

a) All the reactions were carried out at 100 °C in the presence of KF and 1 atm of carbon monoxide in DMI unless otherwise noted. b) Isolated yields. c) The reaction was carried out in DMF. d) This reaction was carried out in the presence of 10 atm of carbon monoxide. e) Reaction carried out at 150 °C.

The reaction temperature and the carbon monoxide pressure also affected the product distribution significantly. When the reaction was carried out under 10 atm of carbon monoxide at 100 °C, 4-acetylbenzoic acid was formed exclusively (entry 9). At 150 °C under 1 atm of CO, on the contrary, the same reaction gave only 4-acetyl-4'-methylbiphenyl (entry 10). The selectivity is governed by the relative rate of CO insertion into Ar-PdIL$_{n-2}$ (path *a*) *vs* transmetalation of a silicate [Ar'SiRF$_3$]$^-$ (path *b*) as shown in Scheme I. Path *b* is obviously preferred at higher temperature and lower carbon monoxide pressure.

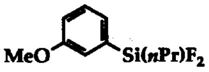
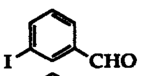
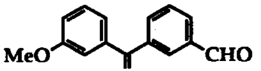
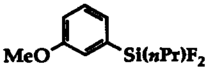
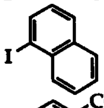
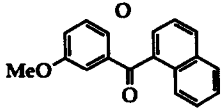
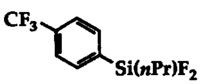
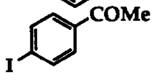
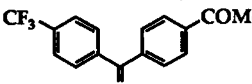
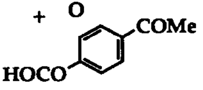
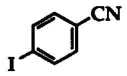
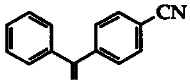
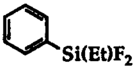
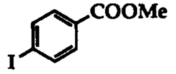
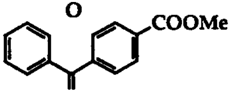
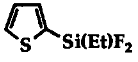
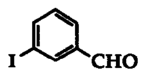
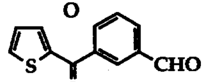
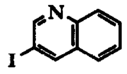
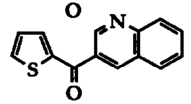
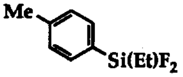
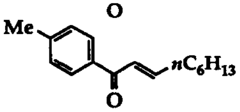
The benzoic acid formed in entries 3, 4, 6, 7, and 9 is apparently derived from the corresponding benzoyl fluoride, which was characterized by ^{19}F NMR of the reaction mixture from entry 9 (δ -26.0 for Ar-CO-*F*, CCl$_3$F as an internal standard). The precursors of Ar-CO-F could be Ar-CO-PdFL$_{n-2}$ and Ar-CO-PdIL$_{n-2}$ (path *c*). This path becomes competitive particularly when the transfer of Ar' from [Ar'SiRF$_3$]$^-$ to Ar-CO-PdIL$_{n-2}$ (path *d*) is slow.

Scheme I



The optimum conditions (1 atm of CO, DMI solvent, KF, (η^3-C$_3$H$_5$PdCl)$_2$ catalyst, 100 °C) were applied to various aryl(alkyl)difluorosilanes and aryl iodides to demonstrate the synthetic versatility of the present method (Table II). The reaction is quite general for substrates possessing not only an electron-donating substituent but an electron-withdrawing one on the aryl ring. Thus, the silicon-based carbonylative coupling offers a short route to a wide range of diaryl ketones substituted by an electronegative group (entries 1, 4, 5, and 6). These ketones are hardly accessible by conventional methods like the Friedel-Crafts reaction. However, the reaction of ethyl(difluoro)(4-trifluoromethylphenyl)silane with 1-(4-iodophenyl)ethanone gave a mixture of 4-acetylbenzoic acid and the desired ketone (entry 3). The strongly electron-withdrawing substituent CF$_3$ should have retarded an electrophilic attack (path *d* in Scheme I) of palladium(II) species to Ar'-Si bond of [Ar'SiRF$_3$]$^-$,[8] thus yielding to carboxylation of the aryl iodide (path *c*).

Table II Pd-Catalyzed Carbonylative Coupling of Arylsilanes[a)]

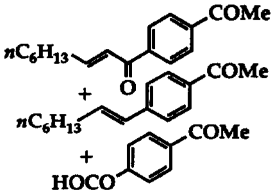
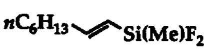
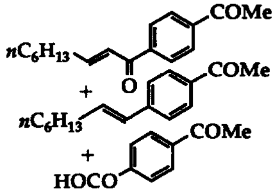
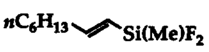
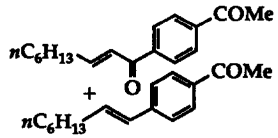
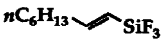
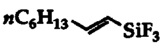
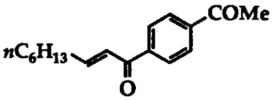
Entry	Arylsilane	Aryl Iodide	Reaction Time (h)	Product(s) (Yield%)[b)]
1			5	 (80)
2			15	 (67)
3			18	 (38) +  (50)
4			5	 (60)
5			5	 (61)
6			6	 (72)
7			19	 (78)
8[c)]			25	 (58)

a) All the reactions were carried out at 100 °C using 1.0 eq of iodide and 1.5 eq of arylsilane under 1 atm of carbon monoxide in the presence of 1.5 eq of potassium fluoride and 2.5 mol% of $(\eta^3\text{-}C_3H_5PdCl)_2$ in DMI unless otherwise noted. b) Isolated yields. c) The reaction was carried out at 50 °C.

Under similar conditions, the carbonylative coupling of (4-methylphenyl)(ethyl)-difluorosilane with (*E*)-1-iodo-1-octene was successfully achieved at 50 °C to afford 1-(4-methylphenyl)-2-nonen-1-one in moderate yield (entry 8).

Carbonylative Coupling of Alkenylfluorosilanes with Aryl and Alkenyl Iodides. To establish the generality of the carbonylative coupling of organofluorosilanes, we studied the reaction of (*E*)-1-silyl-1-octenes, choosing 1-(4-iodophenyl)ethanone as another coupling partner (Table III). The typical conditions (2.5 mol% of $(\eta^3\text{-}C_3H_5PdCl)_2$, 1.0 eq of KF, 1 atm of CO, DMF or DMI as the solvent) was proved to be inappropriate for the reaction of (*E*)-1-

Table III. Pd-Catalyzed Carbonylative Coupling of Octenylsilanes with 1-(4-iodophenyl)ethanone[a)]

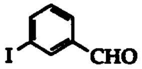
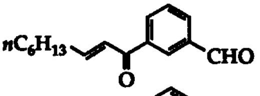
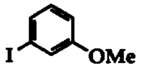
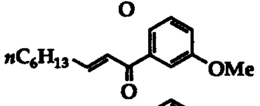
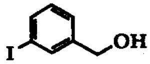
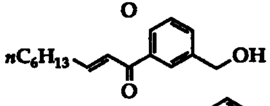
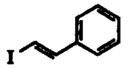
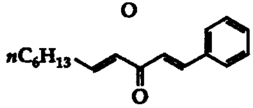
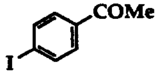
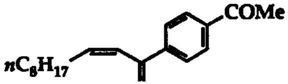
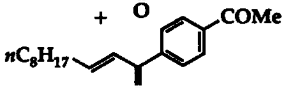
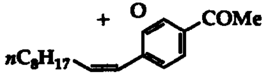
Entry	Alkenylsilane	F^-	Solvent	Reaction Time (h)	Product(s)	(Yield %)[b]
1		KF	DMF	22		14 23 42
2		KF	DMI	48		18 29 38
3		TBAF	THF	12		52 42
4		KF	DMI	2	no reaction	
5		TBAF	THF	22		85

a) All the reactions were carried out at 50 °C using 1 eq of 1-(4-iodophenyl)ethanone and 1.5 eq of 1-octenylsilane in the presence of 2.5 mol% of $(\eta^3\text{-}C_3H_5PdCl)_2$ and 3.0 eq of TBAF or KF in THF under an atmospheric pressure of carbon monoxide. b) Isolated yields are given.

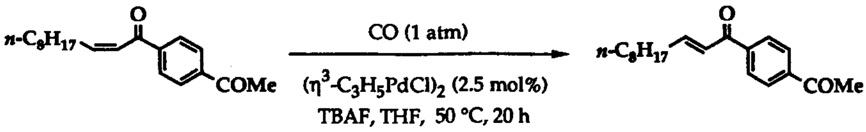
(methyldifluorosilyl)-1-octene: in addition to the desired enone, 4-acetylbenzoic acid and 1-(4-acetylphenyl)-1-octene were produced (entries 1 and 2). (*E*)-1-Trifluorosilyl-1-octene did not give any product (entry 4). Satisfactory results were obtained when tetrahydrofuran (THF) solvent, tetrabutylammonium fluoride (TBAF), and $(\eta^3\text{-}C_3H_5PdCl)_2$ catalyst were employed (entry 5). The efficacy of (*E*)-1-trifluorosilyl-1-octene is surprising, since aryltrifluorosilane did not show any reactivity of the carbonylative coupling (Table I, entry 8).

The optimized conditions were applied to the reaction with various aryl and alkenyl iodides (Table IV). As readily seen, 1-aryl-2-nonen-1-ones were obtained in moderate to good yields (entries 1-3). The *E* configuration of alkenyl iodide and alkenylsilane was maintained in the coupled product (see entries 1-4). However, partial isomerization of *Z* configuration of alkenylsilane was observed (entry 5). The loss of the stereochemistry seems to have occurred after (Z)-enone was produced,[1b] since (Z)-1-(4-acetylphenyl)-2-undecen-1-one was shown to isomerize into the *E* isomer under the carbonylative coupling conditions (eq 3).

Table IV. Pd-Catalyzed Carbonylative Coupling of Octenylsilanes[a)]

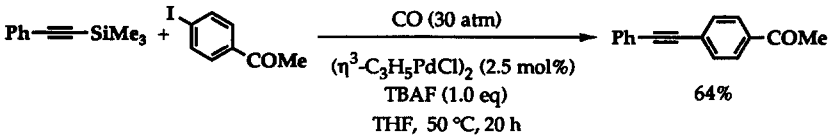
Entry	Alkenylsilane	Aryl Iodide	Reaction Time (h)	Product(s)	(Yield %)[b]
1			17		66
2			17		71
3			17		43
4			20		45
5			12		44
				+ 	26
				+ 	21

a) All the reactions were carried out at 50 °C using 1.0 eq of iodide and 1.5 eq of 1-octenyltrifluorosilane in the presence of 2.5 mol% of $(\eta^3\text{-}C_3H_5PdCl)_2$ and 2.0 eq of TBAF in THF under an atmospheric pressure of carbon monoxide. b) Isolated yields.



(3)

We further studied the possibility of the carbonylative coupling of alkynylsilanes. When 1-phenyl-2-(trimethylsilyl)ethyne was allowed to react with 1-(4-iodophenyl)ethanone under the typical conditions, direct coupling occurred to give 1-(4-acetylphenyl)-2-phenylethyne (cf. eq 4). Under 30 atm of carbon monoxide, the reaction did not give yet detectable amount of a desired alkynyl ketone. This failure may be attributed to extremely rapid alkynyl transfer from silicon to palladium as compared with CO insertion (see Scheme I).



(4)

Conclusion

A wide range of aryl and alkenylfluorosilanes were found to undergo carbonylative coupling with alkenyl and aryl iodides under *1 atm of carbon monoxide* to give diaryl, dialkenyl, and aryl alkenyl ketones in moderate to good yields. Reaction conditions could be found that suppress side reactions such as competitive direct coupling and simple carboxylation of organic halides. High chemoselectivity of the reaction also deserves comment: reactive functional groups like ester, ketone, aldehyde-carbonyl, cyano, and hydroxyl were tolerated under the reaction conditions. Thus, the present method allows the preparation of highly functionalized unsymmetrical ketones in a single operation, starting with organofluorosilanes and various iodides.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Hitachi R-90H (90 MHz) or a Brucker AM-400 (400 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. IR spectra were obtained on a JASCO A-202 spectrometer. Low-resolution mass spectra were obtained on a Hitachi M-80-A spectrometer. Elemental analyses were performed with a Perkin-Elmer 240 instrument.

Solvents DMF and DMI were distilled from calcium hydride and stored over molecular sieves 4 Å. Diethyl ether and THF were freshly distilled from sodium benzophenone ketyl. Preparation of the organosilicon reagents and organic halides were carried out under nitrogen.

Palladium Catalysts and Fluoride Salt. Tetrakis(triphenylphosphine)palladium[9] and dichlorobis(triphenylphosphine)palladium[10] were prepared according to the published procedures. π-Allylpalladium chloride dimer was purchased from Merck; THF solution of tetrabutylammonium fluoride (TBAF) was purchased from Aldrich.

Organic Iodides. Prepared according to the literature were: 3-iodoquinolin,[11] (*E*)-1-iodo-1-octene,[12] and (*E*)-1-iodo-2-phenylethene.[13] 3-Iodobenzaldehyde, 4-iodobenzoic acid, 1-iodonaphthalene, 1-(4-iodophenyl)ethanone, 4-iodo(methoxy)benzene, and 2-(3-

iodophenyl)ethanol are commercially available and used without further purification. 2-(3-Iodophenyl)ethyl acetate was prepared by the reaction of 2-(3-iodophenyl)ethanol with acetyl chloride in the presence of triethylamine in dichloromethane. Methyl 4-iodobenzoate was prepared by the esterification of 4-iodobenzoic acid with excess diazomethane in diethyl ether.

Organosilicon Reagents. Difluoro(methyl)(4-methylphenyl)silane[14] and ethyl(difluoro)-(phenyl)silane[15] were prepared according to the literature procedure. (Trimethyl)(phenyl)-silane, tetraphenylsilane, and phenyltrifluorosilane were purchased from Shinetsu Chem. Co. and used without purification.

Ethyl(difluoro)(4-methylphenyl)silane. To a solution of ethyltrichlorosilane (20.0 g, 120 mmol) in THF (50 mL) was added at 0 °C with stirring 4-methylphenylmagnesium bromide prepared from p-bromotoluene (10.3 g, 60 mmol) and magnesium (1.94 g, 80 mmol) in ether (30 mL). After stirring at room temperature overnight, bulk of the solvent was removed under reduced pressure, and dry hexane was added to the reaction mixture. The resulting slurry was filtered, and the filtrate was concentrated to give a brown oil. Distillation of this oil at 62 °C (0.5 mmHg) afforded dichloro(ethyl)(4-methylphenyl)silane as a colorless oil (7.9 g, 60%): ^{1}H NMR (90 MHz) δ 0.90-1.53 (m, 5 H), 2.42 (s, 3 H), 7.24 (d, J = 8.0 Hz, 2 H), 7.55 (d, J = 8.0 Hz, 2 H). This dichlorosilane was converted to corresponding difluorosilane according to the modified literature procedure.[6] Thus, all of the dichlorosilane was added to anhydrous SbF_3 (8.6 g, 48 mmol) at -70 °C, and the resulting reaction mixture was stirred at room temperature for 2 h. After exothermic reaction ceased, the mixture was heated at 100 °C for 2 h, and cooled to room temperature. The mixture was diluted with hexane (50 mL), and filtered. The filtrate was washed with water (30 mL X 3), and precipitate formed was filtered off. The solution was dried over $MgSO_4$ and concentrated to give (ethyl)(difluoro)(4-methylphenyl)silane as a colorless oil (4.36 g, 65%): bp (bulb-to-bulb) 110 °C (63 mmHg); IR (neat) 1615, 1130, 900, 860, 805, 725 cm^{-1}; ^{1}H NMR (90 MHz) δ 0.90-1.25 (m, 5 H), 2.40 (s, 3 H), 7.24 (d, J = 8.0 Hz, 2 H), 7.56 (d, J = 8.0 Hz, 2 H). Anal. Calcd for $C_9H_{12}SiF_2$: C, 58.03; H, 6.49. Found: C, 57.89; H, 6.52.

Difluoro(3-methoxyphenyl)(propyl)silane. To a solution of 1-(trichlorosilyl)propane (21.3 g, 120 mmol) in THF (50 mL) was added at 0 °C with stirring 3-methoxyphenylmagnesium bromide prepared from 3-methoxyphenyl bromide (11.2 g, 60 mmol) and magnesium (1.94 g, 80 mmol) in diethyl ether (30 mL). After stirring at room temperature overnight, bulk of the solvent was removed under reduced pressure, and dry hexane was added to the reaction mixture. The resulting slurry was filtered, and the filtrate was concentrated to give a brown oil. Distillation at 120 °C (2.0 mmHg) afforded dichloro(3-methoxylphenyl)(propyl)silane as a colorless oil (9.5 g, 64%): ^{1}H NMR (90 MHz) δ 1.0 (t, J = 6.2 Hz, 3 H), 1.15-1.80 (m, 4 H), 3.80 (s, 3 H), 6.92-7.12 (m, 1 H), 7.10 (m, 3 H). Treatment of this dichlorosilane with SbF_3 (9.0 g, 50 mmol) as before[6] gave difluoro(3-methoxyphenyl)(propyl)silane as a colorless oil (5.9 g, 72%): bp (bulb-to-bulb) 110 °C (63 mmHg); IR (neat) 3050, 2980, 1575, 1410, 1240, 1120, 1040, 890, 790, 695 cm^{-1};

^1H NMR (90 MHz) δ 0.80-1.93 (m, 7 H), 3.90 (s, 3 H), 6.88-7.60 (m, 4 H). Anal. Calcd for $C_{10}H_{14}SiF_2O$: C, 55.53; H, 6.52. Found: C, 55. 47; H, 6.58.

Difluoro[(4-trifluoromethyl)phenyl](propyl)silane. Reaction of 1-(trichlorosilyl)propane (21.3 g, 120 mmol) with (4-trifluoromethyl)phenylmagnesium bromide, prepared from (4-trifluoromethyl)phenyl bromide (13.5 g, 120 mmol) and magnesium (1.94 g, 80 mmol) in a way similar to the above , gave dichloro(propyl)[(4-trifluoromethyl)phenyl]silane (9.2 g, 53%): bp 64 °C (0.1 mmHg); ^1H NMR (90 MHz) δ 1.05 (t, J = 6.2 Hz, 3 H), 1.10-1.85 (m, 4 H), 7.54-8.00 (m, 4 H). Fluorination of the dichlorosilane with SbF_3 (7.7 g, 43 mmol)[6] afforded difluoro(propyl)[(4-trifluoromethyl)phenyl]silane as a colorless oil (3.0 g, 37%): bp 45 °C (0.7 mmHg); IR (neat) 3050, 2980, 1310, 1170, 1130, 1060, 905, 860, 830, 740 cm^{-1}; ^1H NMR (90 MHz) δ 0.70-1.24 (m, 5 H), 1.20-1.85 (m, 2 H), 7.50-7.89 (m, 4 H). Anal. Calcd for $C_{10}H_{11}SiF_5$: C, 47.24; H, 4.36. Found: C, 47.20; H, 4.39.

Ethyl(difluoro)(2-thienyl)silane. 2-Thienyllithium,[16] prepared from butyllithium (160 mmol) and thiophene (13.5 g, 160 mmol) in ether (80 mL), was added dropwise to a dry ice-cooled solution of ethyltrichlorosilane (81.8 g, 500 mmol) in ether (300 mL) so slowly that the temperature was kept at -40 °C. The resulting solution was allowed to stand at room temperature overnight. The solvent was removed under reduced pressure, and dry hexane was added to the residue. Filtration of the precipitate, followed by concentration of the filtrate, gave a brown oil. Distillation at 98 °C (13 mmHg) afforded dichloro(ethyl)(2-thienyl)silane as a colorless oil (31.2 g, 92%): ^1H NMR (90 MHz) δ 1.02-1.70 (m, 5 H), 7.25 (dd, J = 3.0, 4.5 Hz, 1 H), 7.55 (dd, J = 3.0, 1.0 Hz, 1 H), 7.75 (dd, J = 1.0, 4.5 Hz, 1 H). This compound was converted with SbF_3 (39 g, 221 mmol) as before[6] into ethyl(difluoro)(2-thienyl)silane (18 g, 68%): colorless oil; bp 62 °C (26 mmHg); IR (neat) 3150, 2900, 1410, 1220, 1100, 1115, 900, 860, 720 cm^{-1}; ^1H NMR (90 MHz) δ 0.90-1.30 (m, 5 H), 7.10-7.35 (m, 1 H), 7.58 (d, J = 4.2 Hz, 1 H), 7.76 (d, J = 5.2 Hz, 1H). Anal. Calcd for $C_6H_8SSiF_2$: C, 40.42; H, 4.52. Found: C, 40. 36; H, 4.65.

(*E*)-1-(Methyldifluorosilyl)-1-octene. Hydrosilylation of 1-octyne (2.7 g, 27 mmol) with methyldichlorosilane (4.6 g, 40 mmol) was carried out using 0.1 mol% of H_2PtCl_6 in 2-propanol (0.2 M, 0.15 mL) at 80 °C according to the literature,[17] giving (*E*)-1-(methyldichlorosilyl)-1-octene as a colorless liquid (5.8 g, 95%): bp 108 °C (14 mmHg); ^1H NMR (90 MHz) δ 0.65-1.05 (m, 3 H), 0.80 (s, 3 H), 1.07-1.70 (m, 8 H), 2.05-2.35 (m, 2 H), 5.77 (d, J = 18 Hz, 1 H), 6.50 (d, J = 18 Hz, 1 H). This was converted to the corresponding difluorosilane according to the literature procedure.[17b] Thus, a solution of the dichlorosilane in diethyl ether (10 mL) was added to suspension of $CuF_2 \cdot 2H_2O$ (3.8 g, 28 mmol) in diethyl ether (10 mL) at 0 °C. After stirring at room temperature overnight, the copper salt was removed by filtration. The filtrate was dried over $MgSO_4$ and concentrated to give (*E*)-1-(methyldifluorosilyl)-1-octene as a colorless oil (3.91 g, 77%): bp 66 °C (15 mmHg); IR (neat) 2950, 1620, 1268, 910, 870, 820 cm^{-1}; ^1H NMR (90 MHz) δ 0.28 (t, J = 5.5 Hz, 3 H), 0.60-1.10 (m, 3 H), 1.06-1.70 (m, 8 H), 2.00-2.30 (m, 2 H), 5.50 (d, J = 21 Hz, 1 H), 6. 48 (dt, J = 21, 6.4 Hz, 1H). Anal. Calcd for $C_9H_{18}SiF_2$: C, 56.21; H, 9.43. Found: C, 56.19; H, 9.48.

(*E*)-1-(Trifluorosilyl)-1-octene. Fluorination of (*E*)-1-(trichlorosilyl)-1-octene[17a] (6.0 g, 24 mmol) with CuF_2 $2H_2O$ (5.0 g, 36 mmol) as before[17b] gave (*E*)-1-(trifluorosilyl)-1-octene (3.1 g, 67%): colorless oil; bp 71 °C (55 mmHg); IR (neat) 2950, 1620, 950, 905, 730 cm^{-1}; ^1H NMR (90 MHz) δ 0.85 (t, J = 6.0 Hz, 3 H), 1.05-1.65 (m, 8 H), 2.00-2.30 (m, 2 H), 5.32 (dq, J = 21, 2.0 Hz, 1 H), 6.70 (dt, J = 21, 6.2 Hz, 1 H). Anal. Calcd for $C_8H_{15}SiF_3$: C, 48.95; H, 7.74. Found: C, 48. 82; H, 7.68.

(Z)-1-(Trifluorosilyl)-1-decene. A solution of (Z)-iodo-1-decene[18] (3.87 g, 14.5 mmol) in THF (25 mL) was slowly added to a dry ice-cooled solution of butyllithium (16 mmol) in hexane (1.60 M). After standing at -70 °C for 30 min, the solution was added to a solution of tetrachlorosilane (8.5 g, 50 mmol) in diethyl ether (50 mL) at room temperature over 15 min. Removal of the solvent and the excess tetrachlorosilane gave crude (Z)-1-(trichlorosilyl)-1-decene, which was treated with $CuF_2 \cdot 2H_2O$ (1.5 g, 8.4 mmol) in diethyl ether as before[17b] to afford (Z)-1-(trifluorosilyl)-1-decene as a colorless oil (0.91 g, 32%): bp (bulb-to-bulb) 70 °C (20 mmHg); IR (neat) 2925, 1610, 1465, 950, 875, 705 cm^{-1}; ^1H NMR (400 MHz) δ 0.85 (t, J = 6.7 Hz, 3 H), 1.02-1.70 (m, 12 H), 2.02-2.40 (m, 2 H), 5.33 (dtq, J = 14.2, 1.5, 4.4 Hz, 1H), 6.86 (m, 1 H). Anal. Calcd for $C_{10}H_{19}SiF_3$: C, 53.54; H, 8.54. Found: C, 53.48; H, 8.60.

General Procedure for Palladium-Catalyzed Carbonylative Coupling Reaction of Arylfluorosilanes with Aryl Iodides (Tables I and II).

4-Acetylphenyl 4-methylphenyl ketone (Table I, entry 2). To a suspension of KF (190 mg, 3.3 mmol), $(\eta^3\text{-}C_3H_5PdCl)_2$ (18 mg, 2.5 mol%), and 1-(4-iodophenyl)ethanone (490 mg, 2.0 mmol) in DMI (10 mL) was added difluoro(ethyl)(4-methylphenyl)silane (560 mg, 3.0 mmol) under 1 atm of carbon monoxide (balloon). After stirring at room temperature for 10 min, the reaction mixture was heated at 100 °C for 3 h. Bulk of the solvent and the catalyst were removed by passing the mixture through a silica gel column with ethyl acetate-hexane = 1 : 10 as an eluent solvent. Evaporation of the solvent under reduced pressure afforded 4-acetylphenyl 4-methylphenyl ketone as a colorless solid (430 mg, 91%): mp 111-112 °C (cyclohexane); IR (KBr) 1690, 1645, 1605, 860, 760, 680 cm^{-1}; ^1H NMR (90 MHz) δ 2.45 (s, 3 H), 2.65 (s, 3 H), 7.20 (d, J = 7.5 Hz, 2 H), 7.70 (d, J = 7.5 Hz, 2 H), 7.82 (d, J = 8.0 Hz, 2 H), 8.04 (d, J = 8.0 Hz, 2 H). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80. 65; H, 5.92. Found: C, 80.61; H, 5.95.

Followings were prepared according to the general procedure.

3-Formylphenyl 3-methoxyphenyl ketone (Table II, entry 1): viscous oil; IR (neat) 3100, 2825, 1700, 1660, 1290, 1040, 800, 740 cm^{-1}; ^1H NMR (90 MHz) δ 3.92 (s, 3 H), 7.04-7.80 (m, 5 H), 8.00-8.37 (m, 3 H), 10. 08 (s, 1 H). Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 74. 93; H, 5.09.

3-Methoxyphenyl 1-naphthyl ketone (Table II, entry 2): viscous oil; IR (neat) 3100, 2950, 1660, 1590, 1585, 1035, 780, 745 cm^{-1}; ^{1}H NMR (90 MHz) δ 3.80 (s, 3 H), 7.05-7.77 (m, 8 H), 7.80-8.25 (m, 3 H). Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.38; H, 5.41.

4-Acetylphenyl 4-(trifluoromethyl)phenyl ketone (Table II, entry 3): colorless solid; mp 133-135 °C (cyclohexane); IR (KBr) 1694, 1655, 1180, 1135, 1070, 935, 865, 775, 680 cm^{-1}; ^{1}H NMR (200 MHz) δ 2.67 (s, 3 H), 7.78 (d, J = 8.38 Hz, 2 H), 7.87 (d, J = 6.53 Hz, 2 H), 7.91 (d, J = 6.53 Hz, 2 H), 8.07 (d, J = 8.38 Hz, 2 H). Anal. Calcd for $C_{16}H_{11}O_2F_3$: C, 65.76; H, 3.79. Found: C, 65.71; H, 3.82. **4-Acetylbenzoic acid**: colorless solid; mp 206-208 °C; IR (Nujol) 2920, 1680, 1505, 1406, 1293, 965, 869, 773, 730, 643 cm^{-1}; ^{1}H NMR (90 MHz) d 2.68 (s, 3 H), 8.05 (d, J = 9.1 Hz, 2 H), 8.23 (d, J = 9.1 Hz, 2 H), 14.5 (br s, 1 H). These spectral data were identical to those of an authentic sample.

4-Cyanobenzophenone (Table II, entry 4): colorless solid; mp 106-108 °C (methanol), lit.[19] 107-108 °C; IR (KBr) 2250, 1650, 1600, 1320, 1280, 858, 800, 740, 680 cm^{-1}; ^{1}H NMR (90 MHz) δ 7.20-8.00 (m, 9 H).

Methyl 4-benzoylbenzoate (Table II, entry 5): colorless solid; mp 108-109 °C (cyclohexane), lit.[20] 107-108 °C; IR (KBr) 3000, 2950, 1710, 1640, 1435, 1275, 1100, 770, 710, 690 cm^{-1}; ^{1}H NMR (90 MHz) δ 3.90 (s, 3 H), 7.30-7.70 (m, 5 H), 7.84 (d, J = 8.2 Hz, 2 H), 8.15 (d, J = 8.2 Hz, 2 H).

3-Formylphenyl 2-thienyl ketone (Table II, entry 6): colorless solid; mp 87-88 °C (cyclohexane); IR (KBr) 3100, 2850, 1700, 1620, 1410, 1310, 1200, 1120, 1055, 720 cm^{-1}; ^{1}H NMR (90 MHz) δ 6.58-8.63 (m, 7 H), 10.2 (s, 1 H). Anal. Calcd for $C_{12}H_8O_2S$: C, 66.65; H, 3.73. Found: C, 66.59; H, 3.75.

2-Thienyl 3-quinolinyl ketone (Table II, entry 7): colorless solid; mp 94-95 °C (cyclohexane); IR (KBr) 3050, 1630, 1590, 1410, 1290, 1250 cm^{-1}; ^{1}H NMR (90 MHz) δ 7.18 (m, 1 H), 7.50-8.05 (m, 5 H), 8.20 (m, 1 H), 8.65 (m, 1 H), 9.35 (m, 1 H). Anal. Calcd for $C_{14}H_9NOS$: C, 70.27; H, 3.79. Found: C, 70.21; H, 3.82.

(*E*)-1-(4-Methylphenyl)-2-nonen-1-one (Table II, entry 8): colorless oil: IR (neat) 2950, 1700, 1670, 1650, 1620, 1290, 980, 810 cm^{-1}; ^{1}H NMR (90 MHz) δ 0.70-1.09 (m, 3 H), 1.11-1.73 (m, 8 H), 2.01-2.36 (m, 2 H), 2.41 (s, 3 H), 6.35 (d, J = 15 Hz, 1 H), 6.95 (dt, J = 15, 6.2 Hz, 1 H), 7.35 (d, J = 7.5 Hz, 2 H), 7.85 (d, J = 7.5 Hz, 1 H). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.38; H, 9.71.

General Procedure for Palladium-Catalyzed Carbonylative Coupling of Alkenylfluorosilanes with Organic Iodides (Tables III and IV).

(*E*)-1-(4-Acetylphenyl)-2-nonen-1-one (Table III, entry 5). To a THF (1.5 mL) solution of 1-(4-iodophenyl)ethanone (49 mg, 0.20 mmol), 1-(trifluorosilyl)-1-octene (59 mg, 0.30 mmol), and (η^3-$C_3H_5PdCl)_2$ (1.8 mg, 2.5 mol%) was added a THF (0.3 mL) solution of TBAF (1.0 M, 0.30

mmol) under 1 atm of carbon monoxide (balloon). After heating at 50 °C for 10 h, the reaction mixture was cooled to room temperature, and an additional TBAF (0.15 mmol) was introduced. After further heating at 50 °C for 12 h, the solvent was removed under reduced pressure to give a crude product. Purification by silica gel column chromatography with hexane-diethyl ether (10 : 1) afforded 1-(4-acetylphenyl)-2-nonen-1-one as a colorless solid (44 mg, 85%): mp 48-50 °C; IR (KBr) 2950, 1680, 1620, 1115, 1005, 960, 820 cm^{-1}; ^{1}H NMR (90 MHz) δ 0.73-1.03 (m, 3 H), 1.16-1.80 (m, 8 H), 2.07-2.40 (m, 2 H), 2.64 (s, 3 H), 6.85 (d, J = 17 Hz, 1 H), 6.90-7.15 (m, 1 H), 8.00 (br s, 4 H). Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.96; H, 8.61.

Followings were prepared according to the general procedure.

(*E*)-1-(3-Formylphenyl)-2-nonen-1-one (Table VI, entry 1): colorless oil; IR (neat) 2950, 1710, 1680, 1620, 1160, 800 cm^{-1}; ^{1}H NMR (90 MHz) δ 0.60-1.03 (m, 3 H), 1.15-1.81 (m, 8 H), 2.12-2.55 (m, 2 H), 6.92 (d, J = 18 Hz, 1 H), 7.00-8.53 (m, 5 H), 10. 1 (s, 1 H). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.59; H, 8.28.

(*E*)-1-(3-Methoxyphenyl)-2-nonen-1-one (Table VI, entry 2): colorless oil: IR (neat) 2875, 1680, 1625, 1260, 1035, 780 cm^{-1}; ^{1}H NMR (90 MHz) δ 0.70-1.09 (m, 3 H), 1.10-2.05 (m, 8 H), 2.20-2.38 (m, 2 H), 3.84 (s, 3 H), 6.80 (d, J = 17 Hz, 1 H), 7.00-7.94 (m, 5 H). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.98; H, 9.02.

(*E*)-1-[3-(Hydroxymethyl)phenyl]-2-nonen-1-one (Table VI, entry 3): colorless oil; IR (neat) 3450, 2950, 1675, 1620, 1160, 1040, 780, 700 cm^{-1}; ^{1}H NMR (90 MHz) δ 0.67-1.05 (m, 3 H), 1.05-1.76 (m, 8 H), 1.97 (br s, 1 H), 2.02-2.33 (m, 2 H), 4.26 (s, 2 H), 6.84 (d, J = 16 Hz, 1 H), 7.00-8.10 (m, 5 H). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.99; H, 9.04.

(1*E*, 4*E*)-1-Phenyl-1,4-undecadien-3-one (Table VI, entry 4): colorless oil; IR (neat) 2950, 1670, 1640, 1605, 1100, 980, 760, 700 cm^{-1}; ^{1}H NMR (90 MHz) δ 0.74-1.03 (m, 3 H), 1.15-2.02 (m, 8 H), 2.00-2.40 (m, 2 H), 6.40 (d, J = 15 Hz, 1 H), 6.73-7.20 (m, 2 H), 7.25-7.76 (m, 6 H). Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.22; H, 9.19.

(Z)-1-(4-Acetylphenyl)-2-undecen-1-one (Table VI, entry 5): colorless viscous oil: IR (neat) 2875, 1680, 1615, 1270, 1000, 965, 825 cm^{-1}; ^{1}H NMR (90 MHz) δ 0.70-1.00(m, 3 H), 1.10-1.80 (m, 12 H), 2.10-2.30 (m, 2 H), 2.63 (s, 3 H), 6.43 (dt, J = 10.5, 6.5 Hz, 1 H), 6.85 (d, J = 10.5 Hz, 1 H), 8.00 (s, 4 H). Anal. Calcd for $C_{19}H_{26}O_2$: C, 79.68; H, 9.15. Found: C, 79.59; H, 9.17. **(*E*)-1-(4-Acetylphenyl)-2-undecen-1-one**: colorless solid: mp 45-52 °C; IR (KBr) 1675, 1620, 970, 825, 680 cm^{-1} ; ^{1}H NMR (90 MHz) δ 0.75-1.10 (m, 3 H), 1.15-2.00 (m, 12 H), 2.20-2.50 (m, 2 H), 2.65 (s, 3 H), 6.87 (d, J = 18 Hz, 1 H), 6.92-7.20 (m, 1 H), 8.00 (s, 4 H). **(Z)-1-(4-Acetylphenyl)-1-decene**: colorless oil: IR (neat) 2925, 1683, 1603, 1265, 850, 590 cm^{-1}; ^{1}H NMR (90 MHz) δ 0.67-1.05 (m, 3 H), 1.05-1.76 (m, 12 H), 2.10-2.45 (m, 2 H), 2.55 (s, 3 H), 5.75 (dt, J = 10.5, 6.6 Hz, 1 H), 6.43 (d, J = 10.5 Hz, 1 H), 7.30 (d, J = 12 Hz, 2 H), 7.95 (d, J = 12 Hz, 2 H).

1-(4-Acetylphenyl)-2-phenylethyne: colorless solid; mp 97-98 °C , lit.[21] 98-98.5 °C; IR (KBr) 2950, 2225, 1685, 1605, 960, 835, 760, 695 cm^{-1}; ^{1}H NMR (90 MHz) δ 2.60 (s, 3 H), 7.02-8.30 (m, 9 H); MS, *m/z* (%) 220 (M$^+$, 46), 205 (52), 176 (37), 43 (100).

References

1. (a) Sheffy, F. K.; Godschlax, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984,** *106,* 4833. (b) Goure, W. F.; Wrghit, M. E.; Davis, P. D.; Labadie, S. S.; Stille, J. K. *J. Am. Chem. Soc.* **1984,** *106,* 6417. (c) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1988,** *110,* 1557. (d) Tanaka, M. *Tetrahedron Lett.* **1979,** 2601. (e) Tanaka, M. *Synthesis* **1981,** 47. (f) Bumajin, N. A.; Bumajina, I. G.; Kashin, N. A.; Beletskaya, I. P. *Dokl. Akad. Nauk. SSSR* **1981,** *261,* 1141. (g) Kikukawa, K.; Idemoto, T.; Katayama, A.; Kono, K.; Wada, F.; Matsuda, T. *J. Chem. Soc., Perkin Trans. 1,* **1987,** 1511.
2. Wakita, Y.; Yasunaga, T.; Kojima, M. *J. Organomet. Chem.* **1985,** *288,* 261.
3. (a) Bumajin, N. A.; Ponomaryov, A. B.; Beletskaya, I. P. *Tetrahedron Lett.* **1985,** *26,* 4819. (b) Wakita, Y.; Yasunaga, T.; Kojima, M. *J. Organomet. Chem.* **1985,** *288,* 261.
4. Larock, R. C.; Hershberger, S. S. *J. Org. Chem.* **1980,** *45,* 3840.
5. (a) Hatanaka, Y.; Ebina, Y.; Hiyama, T. *J. Am. Chem. Soc.* in press. (b) Hatanaka, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1990,** *112,* 7793. (c) Hatanaka, Y.; Fukushima, S.; Hiyama, T. *Chem. Lett.* **1989,** 2049. (d) Hatanaka, Y.; Hiyama, T. *Yuki Gosei Kagaku Kyokai Shi* **1990,** *48,* 834. (e) Hatanaka, Y,; Hiyama, T. *Synlett* in press and the references cited therein.
6. Damrauer, R.; Danahey, S. E. *Organometallics* **1986,** *5,* 1490.
7. Hatanaka, Y.; Hiyama, T. *Chem. Lett.* **1989,** 2049.
8. Voronkov, M. G.; Chernov, N. E.; Perlova, E. M. *J. Organomet. Chem.* **1988,** *341,* 225.
9. Coulson, D. R. *Inorg. Synth.* **1972,** *13,* 121.
10. Tayim, H. A.; Bouldoukian, A.; Award, F. *J. Inorg. Nucl. Chem.* **1970,** *32,* 3799.
11. Leonard, D.; Foster, S. *J. Am. Chem. Soc.* **1952,** *74,* 3671.
12. Zweifel, G.; Whiteney, C. C. *J. Am. Chem. Soc.* **1967,** *89,* 2753.
13. Suzuki, H.; Aihara, M.; Yamamoto, H.; Takamoto, Y.; Ogawa, T. *Synthesis* **1988,** 236.
14. Yen, V. K.; Papovskova, Z.; Schraml, J.; Chvalovsky, V. *Collect. Czech. Chem. Commun.* **1973,** *38,* 3167.
15. Marans, N. S.; Sommer, L. H.; Whitemore, F. C.; *J. Am. Chem. Soc.* **1951,** *73,* 5127.
16. Ramanathan, V.; Levine, R. *J. Org. Chem.* **1962,** *27,* 1667.
17. (a) Tamao, K.; Yoshida, J.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Kumada, M. *Organometallics* **1982,** *1,* 355. (b) Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983,** *39,* 983.
18. Zweifel, G.; Arzoumanian, H. *J. Am. Chem. Soc.* **1967,** *89,* 5086.
19. Bauer, T. Endres, K. *J. Prakt. Chem.* **1913,** *87,* 546.
20. Smith, M. E. *J. Am. Chem. Soc.* **1921,** *43,* 1920.
21. Seyferth, D.; Nestle, M. O.; Wehman, A. T. *J. Am. Chem. Soc.* **1975,** *97,* 7417.