Unusually Accelerated Silylmethyl Transfer from Tin in Stille Coupling: Implication of Coordination-Driven Transmetalation

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Abstract: The palladium-catalyzed cross-coupling reaction of 2-PyMe$_2$SiCH$_2$SnBu$_3$ with aryl iodide (Ar-I) exclusively produced the 2-PyMe$_2$SiCH$_2$ transferred product 2-PyMe$_2$SiCH$_2$Ar. The relative transfer ability of organic group from tin was found to be 2-PyMe$_2$SiCH$_2$ ≫ Ph > Me > Bu ≫ PhMe$_2$SiCH$_2$, which implies the beneficial pyridyl-to-palladium coordination effect. Thus, the transfer of the silylmethyl group from tin to palladium was remarkably accelerated by simply appending the 2-pyridyl group on silicon. The pyridyl-to-palladium coordination was validated in the palladium(II) complex 2-PyMe$_2$SiCH$_2$PdClPPh$_3$ by ^{1}H NMR and X-ray crystal structure analysis. The cross-coupling product was used for further transformations. The C−Si oxidation of the cross-coupling product 2-PyMe$_2$SiCH$_2$Ar afforded ArCH$_2$OH in high yield. The fluoride ion-catalyzed 1,2-addition of 2-PyMe$_2$SiCH$_2$Ar to carbonyl compound (RR′C═O) gave ArCH$_2$C(OH)RR′ in high yield.

Introduction

The palladium-catalyzed cross-coupling reaction of organotin compounds with organic halides (Migita−Kosugi−Stille coupling) has emerged as one of the most important methods for the catalytic carbon−carbon bond formation.[1,2] Noteworthy and advantageous features of this coupling process are that (1) organotin compounds are readily available, (2) organotin compounds are quite air and moisture stable, and (3) cross coupling tolerates a variety of functional groups on either coupling partner. In recent years the Stille coupling has been well recognized as a powerful method for natural product synthesis.[3] Moreover, the cross coupling using aryl chlorides, a long-standing challenge, has been accomplished very recently by utilizing electron-rich and bulky supporting ligands.[4] However, there are still several serious limitations associated with the Stille coupling methodology. While aryl, alkenyl, alkynyl, allyl, and benzyl groups are efficiently transferred into the cross-coupling product, the low transfer ability of the alkyl group from tin has been a bane in this chemistry (Figure 1).[2] For example, synthetically useful silylmethyl groups exhibit extremely low transferring ability and, thus, are not transferred from tin usually. If the silylmethyltin reagents could be effectively cross-coupled with alkenyl or aryl halides, availability of synthetically useful allyl- and benzylsilanes,[5] which bear various functional groups, should be enormously enhanced.[6]

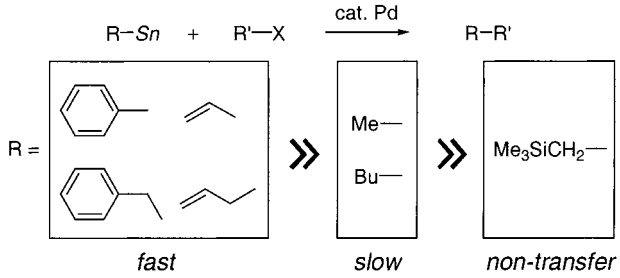

Figure 1. Relative transfer ability of the organic group on tin in Stille coupling.

The low transfer ability of the simple alkyl group from tin has currently been alleviated by several methods. In 1992, Vedejs[7] and Brown[8] have independently discovered that the intramolecular coordination of amine to tin greatly accelerates

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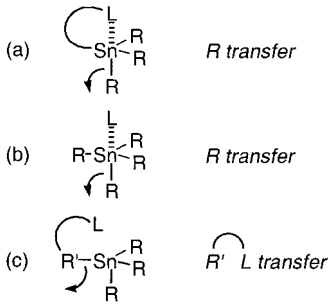
Scheme 1



the transfer of the alkyl group from tin (Scheme 1a).[9] It has been assumed that activation of the alkyl group stems from the coordination-induced alkyl−tin bond elongation.[10] Recently, the activation utilizing externally coordinating ligands such as a fluoride ion has also appeared (Scheme 1b).[11] All these methods are based on the hypervalent organotin strategy.

Recently, we have been engaged in employing the 2-pyridyldimethylsilyl (2-PyMe_2Si) group as an excellent removable intramolecular ligand (directing group) for various metal-catalyzed and -mediated processes.[12,13] We envisioned that the use of the 2-PyMe_2Si group might have some interesting effects on the alkyl group transfer from tin in Stille coupling. During the course of this investigation, we unexpectedly discovered that the 2-PyMe_2SiCH_2 group behaves quite unusually in Stille coupling where the intramolecular ligand (2-PyMe_2SiCH_2 group) itself transfers from tin (Scheme 1c). In this paper, we report on the palladium-catalyzed cross-coupling reaction using 2-PyMe_2-$SiCH_2SnR_3$ with some mechanistic investigations (Scheme 2). Further transformations of the cross-coupling products are also described.

Results and Discussion

Palladium-Catalyzed Cross Coupling of 2-PyMe_2SiCH_2-$SnBu_3$ with Aryl Iodide. Our initial attempt was made by utilizing 2-Py$Me_2SiCH_2SnBu_3$ (**1a**) as a substrate, which can be easily prepared by the reaction of 2-PyMe_2SiCH_2Li with Bu_3-SnCl.[12g] Treatment of **1a** with 1.2 equiv of iodobenzene in the presence of 5 mol % of $PdCl_2(CH_3CN)_2$ and 10 mol % of PPh_3 in THF at 50 °C afforded the coupling product **2a** in 13% yield after 24 h (Table 1, entry 1). Screening of the phosphine ligand revealed that the use of more π-accepting ligands such as $P(C_6H_4CF_3\text{-}4)_3$ and $P(C_6F_5)_3$ provided **2a** in higher yields (entries 2−4). This may be rationalized by assuming that these electron-withdrawing ligands rendered the Ph-Pd$(L)_n$-I intermediate more electrophilic, thereby enhancing the rate of the slow transmetalation step.[14] Similarly, the coupling with 4-iodoacetophenone was found to be more efficient when those ligands were employed (entry 5 vs entries 6 and 7). In all cases, we observed only a trace amount of Bu transferred product in the reaction mixture.

Scheme 2

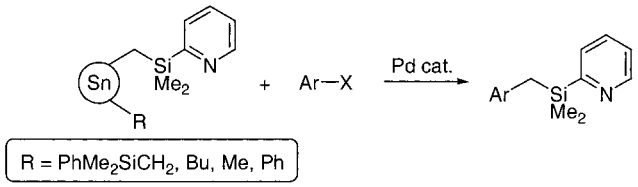
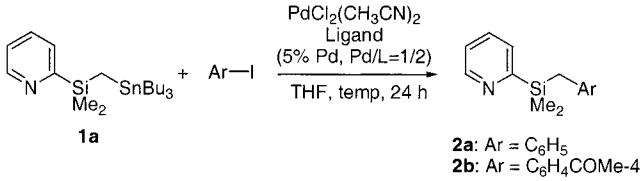
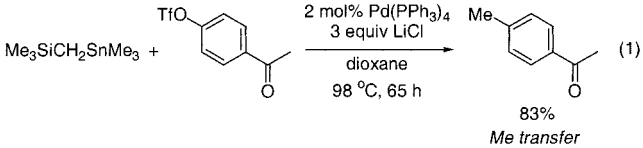


Table 1. Pd-Catalyzed Cross Coupling of **1a** with Aryl Iodide



entry	ligand	temp (°C)	product	yield (%)
1	PPh_3	50	**2a**	13
2	$P(C_6H_4CF_3\text{-}4)_3$	50	**2a**	46
3	$P(C_6H_4CF_3\text{-}4)_3$	70	**2a**	64
4	$P(C_6F_5)_3$	50	**2a**	56
5	PPh_3	50	**2b**	49
6	$P(C_6H_4CF_3\text{-}4)_3$	50	**2b**	76
7	$P(C_6F_5)_3$	50	**2b**	84

It was quite unexpected and interesting to observe that the 2-PyMe_2SiCH_2 group was selectively transferred from tin to give the coupling product with aryl halides. As can be seen in the original report of Stille, the silylmethyl group is one of the hardest groups to transfer from tin in cross coupling.[15] For example, when $Me_3SiCH_2SnMe_3$ is used as an organotin nucleophile, the methyl group is selectively transferred (eq 1).



The use of $(Me_3SiCH_2)_4Sn$ resulted in the recovery of starting material even under forcing conditions.[15] Therefore, under the usual situation, the silylmethyl group can be considered as a "dummy" ligand in Stille coupling.[16] Quite similarly, Bertz has

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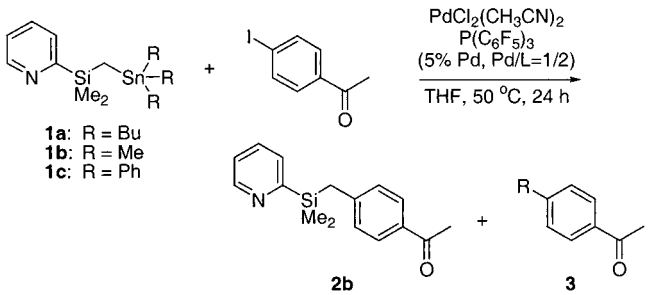
(16) To the best of our knowledge, there is only one example of silylmethyl group transfer from tin in Stille coupling. See ref 7.

Table 2. Pd-Catalyzed Cross Coupling of 2-PyMe$_2$SiCH$_2$SnR$_3$ with 4-Iodoacetophenone



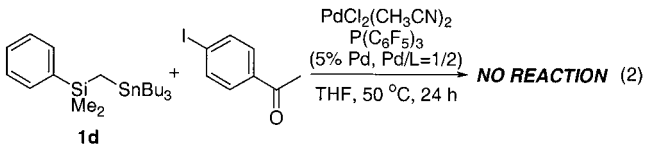
entry	R	yield (%)	**2b**/**3**	relative transfer ability (2-PyMe$_2$SiCH$_2$/R)
1	Bu (**1a**)	87	96/4	99/1
2	Me (**1b**)	52	58/42	81/19
3	Ph (**1c**)	53	45/55	71/29

recently discovered that silylmethyl group serves as an excellent "dummy" ligand in organocuprate chemistry.[17,18]

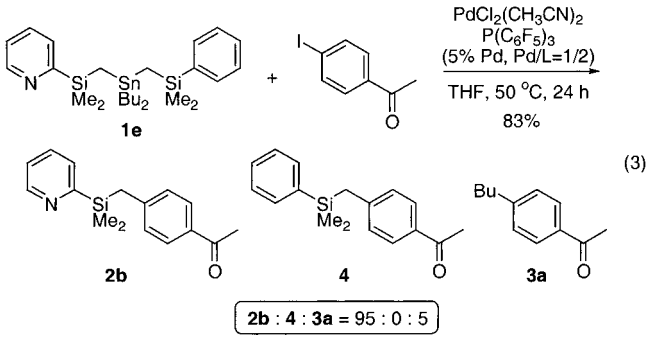
These conspicuous and seminal results (Table 1) clearly brought to light several critical questions which have to be addressed: (1) Why was the Bu group not transferred in our system, (2) how facile does the 2-PyMe$_2$SiCH$_2$ group transfer from tin compared to the other common transferring group, (3) is there any beneficial coordination effect of the pyridyl group during the catalytic cycle, and (4) if so, is the pyridyl group coordinating to tin, as observed by Vedejs and Brown, or coordinating to palladium?

Relative Transfer Ability of the 2-PyMe$_2$SiCH$_2$ Group. Having observed the unusually accelerated 2-PyMe$_2$SiCH$_2$ group transfer, we next set out to compare the relative transfer ability of the 2-PyMe$_2$SiCH$_2$ group with other organic groups (Table 2). The cross coupling was performed by stirring a mixture of 2-PyMe$_2$SiCH$_2$SnR$_3$ (**1a**: R = Bu; **1b**: R = Me; **1c**: R = Ph), 4-iodoacetophenone (1.2 equiv), PdCl$_2$(CH$_3$CN)$_2$ (5 mol %), and P(C$_6$F$_5$)$_3$ (10 mol %) in THF at 50 °C for 24 h. The coupling with **1a** afforded 2-PyMe$_2$SiCH$_2$ transferred product **2b** and Bu transferred product **3a** (entry 1). The ratio of **2b**/**3a** was determined to be 96/4 by ^{1}H NMR analysis. The relative transfer ability of these two groups (2-PyMe$_2$SiCH$_2$ and Bu groups) was determined to be 99/1 by dividing the yield of **2b** or **3** by the number of groups attached on tin (one for **2b** and three for **3**, respectively). Subjection of **1b** and **1c** to the cross coupling afforded the cross-coupling products in 52% and 53% yield, respectively (entries 2 and 3). In both cases, the relative transfer ability of the 2-PyMe$_2$SiCH$_2$ group was found to be greater than that of Me and Ph groups (81/19 and 71/29, respectively). The observed relative transfer ability (2-PyMe$_2$SiCH$_2$ ≫ Ph > Me > Bu) was apparently unusual when considering the previously reported transferring ability order (Ph > Me > Bu ≫ Me$_3$SiCH$_2$).[2]

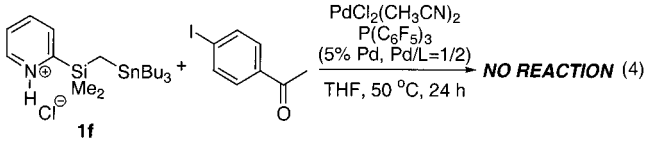
To better ascertain the beneficial effect of the pyridyl group in silylmethyl group transfer, several control experiments were conducted (eqs 2−4). First, PhMe$_2$SiCH$_2$SnBu$_3$ (**1d**) was subjected to cross coupling (eq 2). However, none of the organic



groups including the PhMe$_2$SiCH$_2$ group were transferred under the identical conditions for 2-PyMe$_2$SiCH$_2$SnBu$_3$ (**1a**). Clearly, the pyridyl group in **1a** enhanced not only the selectivity but also the reactivity. The huge transferring ability difference between 2-PyMe$_2$SiCH$_2$ and PhMe$_2$SiCH$_2$ groups can also be observed in the intramolecular competitive reaction with **1e** (eq 3). The 2-PyMe$_2$SiCH$_2$ transferred product **2b** was exclusively



obtained while PhMe$_2$SiCH$_2$ transferred product **4** was not detected at all. We next subjected the hydrochloride of 2-PyMe$_2$SiCH$_2$SnBu$_3$ (**1f**) to cross coupling (eq 4). The coupling product



was not detected at all, presumably due to the blocking of the pyridyl coordination site by protonation. These results clearly suggest that the beneficial effect of the pyridyl group is attributed to the coordinating aptitude to either tin or palladium.

^{119}Sn NMR Study of Organotin Compounds. As already mentioned, Vedejs[7] and Brown[8] have reported that the intramolecular coordination of amine to tin greatly accelerates the transmetalation step (transfer of the organic group from tin to palladium).[19] If the pyridyl group is coordinating to tin in our system, the Bu group instead of the 2-PyMe$_2$SiCH$_2$ group should be selectively transferred from tin (Scheme 1a). Since this is not the case, the pyridyl group is likely not coordinating to tin in our system. To verify if the pyridyl group is coordinating to tin or not in solution, ^{119}Sn NMR spectra of 2-PyMe$_2$SiCH$_2$SnBu$_3$ (**1a**) and PhMe$_2$SiCH$_2$SnBu$_3$ (**1d**) were taken. Organotin **1a** showed resonance at −0.70 ppm in its ^{119}Sn NMR spectrum that is similar to that of **1d** (−0.55 ppm). The minor chemical shift difference seems to support the notion that the complexation of the pyridyl group to tin is not a viable explanation for the selective 2-PyMe$_2$SiCH$_2$ group transfer and for the enormously different reactivities between **1a** and **1d**.

Stoichiometric Reaction of 2-PyMe$_2$SiCH$_2$SnBu$_3$ with Pd(II) Complex. We next conducted the stoichiometric reaction of 2-PyMe$_2$SiCH$_2$SnBu$_3$ (**1a**) with palladium(II) complex. First, **1a** was treated with PhPdI(PPh$_3$)$_2$ to see if the pyridyl group is coordinating to palladium *after* the Sn/Pd transmetalation. However, because of rapid reductive elimination, we obtained the coupling product 2-PyMe$_2$SiCH$_2$Ph (**2a**) instead of the

(17) Bertz, S. H.; Eriksson, M.; Miao, G.; Snyder, J. P. *J. Am. Chem. Soc.* **1996**, *118*, 10906.

(18) The Me$_3$SiCH$_2$ group has received particular attention in the metal alkyl chemistry because of lacking β-hydrogen, thus increasing the stability of alkylmetal complexes: (a) Wilkinson, G. *Pure Appl. Chem.* **1972**, *30*, 627. (b) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Acc. Chem. Res.* **1974**, *7*, 209. (c) Baird, M. C. *J. Organomet. Chem.* **1974**, *64*, 289.

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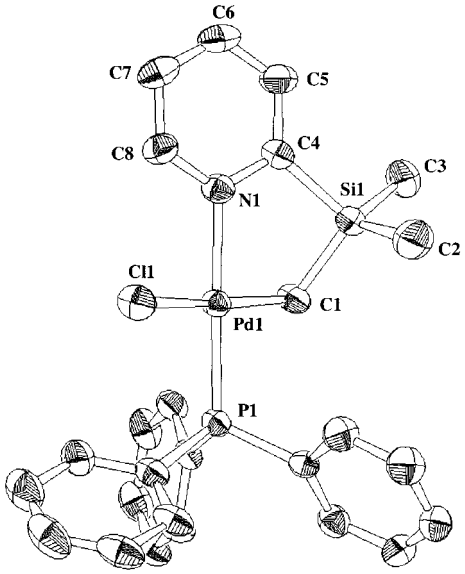
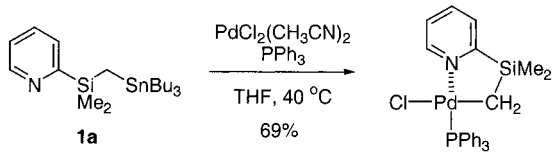


Figure 2. ORTEP drawing of **5**. Thermal ellipsoids are drawn at the 40% probability level and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pd(1)−Cl(1) = 2.392(2), Pd(1)−P(1) = 2.248(2), Pd(1)−N(1) = 2.150(5), Pd(1)−C(1) = 2.088(7), C(1)−Si(1) = 1.873(7), Si(1)−C(4) = 1.900(8), C(4)−N(1) = 1.385(9). Selected bond angles (deg): Cl(1)−Pd(1)−P(1) = 95.46(7), Cl(1)−Pd(1)−N(1) = 90.6(2), N(1)−Pd(1)−C(1) = 86.6(2), C(1)−Pd(1)−P(1) = 87.3(2).

desired bis(organo)palladium(II) complex.[20] Thus, we next examined the stoichiometric reaction of **1a** with $PdCl_2(CH_3CN)_2$ and PPh_3, and the palladium(II) complex **5** was isolated in 69% yield (eq 5).[21] In complex **5**, the coordination of the



(5)

pyridyl group to palladium was highly indicated by the noticeable changes of the pyridine ring chemical shift in the ^{1}H NMR spectrum (see the Experimental Section).[22]

X-ray Crystal Structure of 5. The molecular structure of **5**, determined by X-ray crystallographic analysis, revealed the coordination of the pyridyl group to palladium (Figure 2). The palladium has a square-planar geometry and PPh_3 sits trans to the pyridyl group. Interestingly, the pyridine ring deviates from the coordination plane (tortion angle C(1)−Pd(1)−N(1)−C(4) = −26.3°) presumably because of the envelope-like conformation of five-membered metallacycle (C−Pd−N−C−Si). From these data, it might be reasonable to presume that the pyridyl-to-palladium coordination is a driving force for the facile 2-$PyMe_2SiCH_2$ group transfer.[23]

Mechanistic Rationale Based on Pyridyl-to-Palladium Coordination. On the basis of the ^{119}Sn NMR study, it is reasonable to conclude that the pyridyl group is not coordinating to tin in the cross coupling with **1a** as an organotin nucleophile. Instead, we favor the mechanistic rationale based on the pyridyl-to-palladium coordination at the transmetalation step (Figure 3). Although the mechanism of the transmetalation step is still uncertain,[24] there are two major pathways proposed for this step, namely the S_E2(cyclic) mechanism (intermediate **A**)[25,26] and the S_E2(open) mechanism (intermediate **B**).[27] Very recently, Espinet has proposed that the S_E2(cyclic)-type mechanism fits for the palladium-catalyzed cross-coupling reaction of organotin compound with aryl iodide in THF based on the kinetic studies on catalytic reactions, and on the reactions with isolated intermediates.[26] Thus we favor the S_E2(cyclic)-type mechanism for the cross-coupling reaction with 2-$PyMe_2SiCH_2SnBu_3$ at the present time. Whichever mechanism is operating, the coordination of the pyridyl group to palladium brings tin into the proximity of the palladium and renders the subsequent transmetalation intramolecular in nature, thereby facilitating the transfer of the bridging 2-$PyMe_2SiCH_2$ group (**A** or **B**). Although experimental evidence was not provided, similar coordination effects were proposed in the alkenyl group transfer from tin by several groups.[28] In addition to this kinetic preference, stabilization of the palladium(II) intermediate (**C**) by complexation with the pyridyl group might also contribute to accelerate the 2-$PyMe_2SiCH_2$ group transfer. A similar coordination effect was proposed in the Cu-catalyzed cross-coupling reaction of α-heteroatom-substituted organotin compounds.[29]

Transformations of Coupling Product. The cross-coupling product **2** can be used for further transformations (Scheme 3). We have already reported that the 2-$PyMe_2Si$ group can be converted to the hydroxyl group by the H_2O_2/KF system.[30,31] By using this protocol, **2a** can be converted into the corresponding alcohol **6a** in 94% yield (Scheme 3). By combining this C−Si oxidation with the Stille coupling, the overall process can be regarded as a nucleophilic hydroxymethylation of aryl halides.[32] It should be mentioned that such processes have emerged as important transformations in natural product syn-

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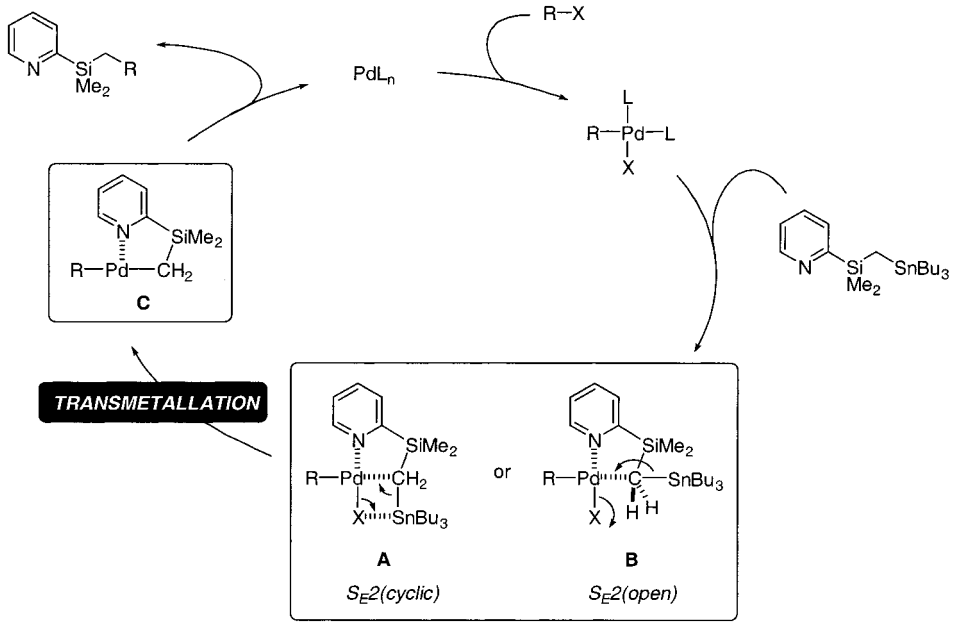
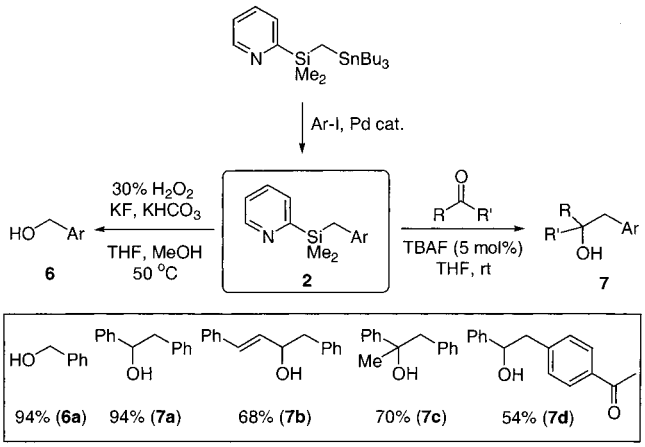


Figure 3. Pyridyl-to-palladium coordination at the transmetalation step.

Scheme 3



thesis.[33] Moreover, this procedure may have some advantages over the direct hydroxymethylation with Bu_3SnCH_2OH,[34] because the Bu_3SnCH_2OH protocol often requires the use of HMPA as a solvent and suffers from the occurrence of considerable Bu group transfer.[35]

The fluoride ion-catalyzed addition of **2** to carbonyl compound was found to take place giving alcohol **7** in high yield (Scheme 3).[36] Not only simple aldehydes, but also α,β-unsaturated aldehydes and ketones were found to be good electrophiles in this reaction. In the case of α,β-unsaturated aldehyde, we observed only the 1,2-addition product **7b**.

Conclusion

In summary, we have found that the transfer of the synthetically useful silylmethyl group from tin to palladium was remarkably accelerated by simply appending the 2-pyridyl group on silicon. This appears to be the general and practical silylmethyl group transfer from tin in Stille coupling. The relative transfer ability of the organic group was found to be $2\text{-PyMe}_2\text{SiCH}_2 \gg \text{Ph} > \text{Me} > \text{Bu} \gg \text{PhMe}_2\text{SiCH}_2$, which implies the beneficial pyridyl-to-palladium coordination effect. The pyridyl-to-palladium coordination was validated in the transmetalated palladium complex **5** by ^{1}H NMR and X-ray crystal structure analysis. Further transformations of the coupling product clearly augment the synthetic utility of the cross coupling using $2\text{-PyMe}_2\text{SiCH}_2\text{SnBu}_3$. The utility of $2\text{-PyMe}_2\text{SiCH}_2\text{SnBu}_3$ as synthons, its ease of preparation (two steps from 2-bromopyridine), and the resultant opportunity for sequential reactions distinguish this chemistry and suggest multiple possibilities for further development. Moreover, we believe that the coordination-driven transmetalation demonstrated herein may be a useful alternative to the hypervalent organotin strategy for enhancing the transfer of otherwise nontransferring organic groups from tin in Stille coupling. If this goal could be accomplished, the utility of Stille coupling methodology will be enormously heightened.

Experimental Section

General. ^{1}H, ^{13}C, ^{31}P, and ^{119}Sn NMR spectra were recorded on Varian GEMINI-2000 (^{1}H 300 MHz, ^{13}C 75 MHz), JEOL A-500 (^{1}H 500 MHz, ^{13}C 125 MHz), and JEOL A-400 (^{31}P 162 MHz, ^{119}Sn 149 MHz) spectrometers in $CDCl_3$ with chemical shifts referenced to internal standards (7.26 ppm ^{1}H, 77.0 ppm ^{13}C), H_3PO_4 (0 ppm), or Me_4Sn (0 ppm). EI mass spectra were recorded on a JMS-SX102A spectrometer. FAB mass spectra were recorded on a JMS-HX110A spectrometer. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were freshly distilled under argon from sodium benzophenone ketyl prior to use. 2-Pyridyltrimethylsilane was prepared according to the literature procedures.[37]

[(2-Pyridyldimethylsilyl)methyl]tributylstannane (1a). To a solution of 2-pyridyltrimethylsilane (5.56 g, 36.8 mmol) in dry Et_2O (50 mL) was added dropwise a solution of *t*-BuLi (40.4 mmol, 1.37 M solution in pentane) at −78 °C under argon. The mixture was stirred

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for an additional 45 min to afford an orange ether solution of (2-pyridyldimethylsilyl)methyllithium. To this solution was added a solution of chlorotributylstannane (15.6 g, 47.8 mmol) in Et_2O (20 mL) at −78 °C. After being stirred at room temperature for 12 h, the reaction mixture was quenched with H_2O (50 mL). The aqueous phase was extracted with Et_2O (2 × 50 mL), and the combined organic phase was washed with H_2O (50 mL). Drying over $MgSO_4$ and subsequent silica gel chromatography (hexane/EtOAc = 20/1 to 10/1) afforded **1a** (12.1 g, 74%) as colorless oil:^{1}H NMR (300 MHz) δ −0.01 (s, J_{Sn-H} = 65.1 Hz, 2 H), 0.31 (s, 6 H), 0.70−0.78 (m, 6 H), 0.85 (t, J = 7.2 Hz, 9 H), 1.18−1.50 (m, 12 H), 7.15 (ddd, J = 7.5, 5.1, 1.8 Hz, 1 H), 7.49 (dm, J = 7.5 Hz, 1 H), 7.55 (td, J = 7.5, 1.5 Hz, 1 H), 8.75 (dm, J = 5.1 Hz, 1 H); ^{13}C NMR (75 MHz) δ −9.5, −0.5, 10.2, 13.5, 27.3, 29.0, 122.5, 128.6, 133.9, 150.1, 169.9; ^{119}Sn NMR (149 MHz) δ −0.70. IR (neat) 1576, 1559, 1464, 1456, 1418, 1375, 1246, 1138 cm^{-1}. HRMS (FAB) *m*/*z* calcd for $C_{20}H_{40}NSiSn$ (M + H)$^+$: 440.1952. Found: 440.1955. Anal. Calcd for $C_{20}H_{39}NSiSn$: C, 54.55; H, 8.93; N, 3.18. Found: C, 54.39; H, 9.20; N, 3.25.

[(2-Pyridyldimethylsilyl)methyl]trimethylstannane (1b). The title compound was prepared by a similar procedure to that used for **1a** (83%). ^{1}H NMR (300 MHz) δ 0.01 (s, J_{Sn-H} = 54.0 Hz, 9 H), 0.06 (s, 2 H), 0.31 (s, 6 H), 7.16 (ddd, J = 7.5, 5.1, 1.8 Hz, 1 H), 7.49 (ddd, J = 7.5, 1.8, 1.5 Hz, 1 H), 7.56 (td, J = 7.5, 1.8 Hz, 1 H), 8.75 (ddd, J = 5.1, 1.8, 1.5 Hz, 1 H); ^{13}C NMR (75 MHz) δ −8.0, −6.4, −0.6, 122.5, 128.4, 133.8, 149.9, 169.3. IR (neat) 1576, 1246 cm^{-1}. HRMS (FAB) *m*/*z* calcd for $C_{11}H_{22}NSiSn$ (M + H)$^+$: 316.0537. Found: 316.0547.

[(2-Pyridyldimethylsilyl)methyl]triphenylstannane (1c). The title compound was prepared by a similar procedure to that used for **1a** (67%). ^{1}H NMR (300 MHz) δ 0.28 (s, 6 H), 0.78 (s, J_{Sn-H} = 74.4 Hz, 2 H), 7.10 (ddd, J = 7.2, 4.8, 1.5 Hz, 1 H), 7.32−7.36 (m, 9 H), 7.46 (td, J = 7.8, 1.8 Hz, 1 H), 7.51−7.54 (m, 6 H), 7.59−7.62 (m, 1 H), 8.59 (dm, J = 4.8 Hz, 1 H); ^{13}C NMR (75 MHz) δ −7.1, −0.5, 122.7, 128.2 (J_{Sn-C} = 50.1 Hz), 128.5, 128.6, 133.8, 136.8 (J_{Sn-C} = 36.5 Hz), 140.1, 149.7, 168.1. IR (neat) 1428, 1246, 1075, 1001 cm^{-1}. HRMS (EI) *m*/*z* calcd for $C_{26}H_{27}NSiSn$: 501.0940. Found: 501.0930.

[(Phenyldimethylsilyl)methyl]tributylstannane (1d). To a solution of chlorotributylstannane (1.56 g, 4.79 mmol) in Et_2O (1.0 mL) was added a solution of $PhMe_2SiCH_2MgCl$ (5.0 mmol, 2.77 M in Et_2O, prepared by the reaction of $PhMe_2SiCH_2Cl$ with Mg). After the mixture was stirred at room temperature for 7 h, H_2O (3.0 mL) was added to the mixture. The aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic phase was dried over $MgSO_4$. Removal of solvents under reduced pressure and subsequent silica gel chromatography (hexane) afforded **1d** (2.11 g, quant) as a colorless oil:^{1}H NMR (300 MHz) δ −0.07 (s, J_{Sn-H} = 65.4 Hz, 2 H), 0.27 (s, 6 H), 0.75 (t, J = 8.1 Hz, J_{Sn-H} = 50.4 Hz, 6 H), 0.86 (t, J = 7.5 Hz, 9 H), 1.19−1.31 (m, 6 H), 1.34−1.44 (m, 6 H), 7.33−7.35 (m, 3 H), 7.51−7.54 (m, 2 H); ^{13}C NMR (75 MHz) δ −8.6, 0.2, 10.2, 13.7, 27.4, 29.1, 127.6, 128.5, 133.2, 141.9; ^{119}Sn NMR (149 MHz) δ −0.55. IR (neat) 1248, 1113, 833, 814 cm^{-1}. HRMS (FAB) *m*/*z* calcd for $C_{20}H_{37}SiSn$ (M − CH_3)$^+$: 425.1687. Found: 425.1683.

[(2-Pyridyldimethylsilyl)methyl][(phenyldimethylsilyl)methyl]-dibutylstannane (1e). To a solution of dichlorodibutylstannane (1.51 g, 5.0 mmol) in Et_2O (3.0 mL) was added a solution of $PhMe_2SiCH_2$-MgCl (5.0 mmol, 2.77 M in Et_2O) at 0 °C, and the mixture was stirred at room temperature for 5 h. To this mixture was added a solution of 2-$PyMe_2SiCH_2Li$ (5.1 mmol) in Et_2O at −78 °C. After the mixture was stirred for 3 h, H_2O (10 mL) was added. The aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic phase was dried over $MgSO_4$. Removal of solvents under reduced pressure and subsequent silica gel chromatography (hexane/EtOAc = 10/1) afforded **1e** (568 mg, 22%) as a colorless oil: ^{1}H NMR (300 MHz) δ −0.07 (s, J_{Sn-H} = 67.5 Hz, 2 H), −0.01 (s, J_{Sn-H} = 66.6 Hz, 2 H), 0.25 (s, 6 H), 0.31 (s, 6 H), 0.67 (t, J = 7.8 Hz, 4 H), 0.82 (t, J = 7.2 Hz, 6 H), 1.12−1.32 (m, 8 H), 7.18 (ddd, J = 7.5, 4.8, 1.5 Hz, 1 H), 7.30−7.34 (m, 3 H), 7.46−7.51 (m, 3 H), 7.57 (td, J = 7.5, 1.8 Hz, 1 H), 8.75 (ddd, J = 4.8, 1.8, 1.2 Hz, 1 H); ^{13}C NMR (125 MHz) δ −7.4, −6.5, −0.3, 0.3, 11.9, 13.6, 27.3 (J_{C-Sn} = 66.5 Hz), 28.9 (J_{C-Sn} = 20.0 Hz), 122.5, 127.6, 128.5, 128.6, 133.2, 134.0, 141.8, 149.8, 169.4. IR (neat) 1246, 1113, 990, 816 cm^{-1}. HRMS (FAB) *m*/*z* calcd for $C_{25}H_{43}NSi_2Sn_2$ (M + H)$^+$: 534.2039. Found: 534.2023.

[(2-Pyridyldimethylsilyl)methyl]tributylstannane Hydrochloride (1f). To **1a** (213.5 mg, 0.48 mmol) was added HCl solution in Et_2O (5 mL, 1 M, 5 mmol) at room temperature. After being stirred for 5 min, the mixture was filtered. Drying the residue under reduced pressure afforded **1f** (229 mg, quant) as a colorless solid: ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.22 (s, J_{Sn-H} = 63.0 Hz, 2 H), 0.44 (s, 6 H), 0.76−0.88 (m, 15 H), 1.18−1.30 (m, 6 H), 1.30−1.46 (m, 6 H), 7.68 (d, J = 7.1 Hz, 1 H), 8.04 (t, J = 6.8 Hz, 1 H), 8.19 (d, J = 7.5 Hz, 1 H), 8.51 (t, J = 7.2 Hz, 1 H), 8.94 (d, J = 5.3 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ −10.1, −0.9, 10.0, 13.5, 26.6 (J_{C-Sn} = 56.2 Hz), 28.4, 126.8, 132.5, 143.1, 143.9, 161.5.

Procedure for the Palladium-Catalyzed Cross Coupling of 1 with 4-Iodoacetophenone (Table 2, Entry 1). To a solution of $PdCl_2(CH_3CN)_2$ (4.1 mg, 0.016 mmol, 5 mol %) and $P(C_6F_5)_3$ (16.9 mg, 0.032 mmol, 10 mol %) in THF (1.0 mL) were added **1a** (145.0 mg, 0.33 mmol), 4-iodoacetophenone (93.6 mg, 0.38 mmol), and THF (1.0 mL). After the mixture was stirred at 50 °C for 24 h, 1,8-diazabicyclo[5.4.0]-undec-7-ene (ca. 0.1 mL) and Et_2O (1.0 mL) were added to the mixture. The catalyst and tin residue were removed by filtration through a short silica gel pad (EtOAc). The filtrate was evaporated to give the crude product. The yield of **2b** and **3a** was determined to be 87%, with the ratio of 96/4, as judged by ^{1}H NMR analysis with phenyl acetate as an internal standard. Compound **2b** was isolated in a pure form by the acid−base extraction as follows. The solution of a crude mixture in Et_2O (2 mL) was extracted with 1 N aqueous HCl (5 × 1 mL). The combined aqueous phase was neutralized by adding $NaHCO_3$ and then was extracted with EtOAc (3 × 20 mL). Drying over $MgSO_4$ and removal of solvents under reduced pressure afforded **2b** (72.7 mg, 82%) as a pale yellow oil.

4-[(2-Pyridyldimethylsilyl)methyl]acetophenone (2b). ^{1}H NMR (300 MHz) δ 0.31 (s, 6 H), 2.51 (s, 2 H), 2.54 (s, 3 H), 7.00 (d, J = 8.1 Hz, 2 H), 7.25 (ddd, J = 7.5, 4.8, 1.2 Hz, 1 H), 7.38 (dt, J = 7.5, 1.2 Hz, 1 H), 7.59 (td, J = 7.5, 1.2 Hz, 1 H), 7.76 (dt, J = 8.4, 1.8 Hz, 2 H), 8.81 (ddd, J = 4.8, 1.5, 1.2 Hz, 1 H); ^{13}C NMR (75 MHz) δ −4.1, 25.8, 26.4, 123.1, 128.2, 128.4, 129.4, 133.4, 134.1, 146.3, 150.1, 165.7, 197.8. IR (neat) 1680, 1603, 1271 cm^{-1}. HRMS (EI) *m*/*z* calcd for $C_{16}H_{19}NOSi$: 269.1236. Found: 269.1232. Anal. Calcd for $C_{16}H_{19}NOSi$: C, 71.33; H, 7.11; N, 5.20. Found: C, 71.16; H, 7.13; N, 5.11.

[(2-Pyridyldimethylsilyl)methyl]benzene (2a). ^{1}H NMR (300 MHz) δ 0.31 (s, 6 H), 2.42 (s, 2 H), 6.97 (dm, J = 7.5 Hz, 2 H), 7.02−7.09 (m, 1 H), 7.12−7.24 (m, 3 H), 7.40 (dm, J = 7.5 Hz, 1 H), 7.55 (td, J = 7.5, 1.5 Hz, 1 H), 8.82 (dm, J = 5.1 Hz, 1 H); ^{13}C NMR (75 MHz) δ −4.2, 24.8, 122.9, 124.1, 128.2, 128.3, 129.4, 134.0, 139.6, 150.2, 166.8. IR (neat) 1599, 1574, 1493, 1451, 1418, 1248, 1208 cm^{-1}. HRMS (EI) *m*/*z* calcd for $C_{14}H_{17}NSi$: 227.1130. Found 227.1129. Anal. Calcd for $C_{14}H_{17}NSi$: C, 73.95; H, 7.54; N, 6.16. Found: C, 74.05; H, 7.61; N, 6.10.

Palladium Complex 5. To a solution of $PdCl_2(CH_3CN)_2$ (78.0 mg, 0.30 mmol) in THF (2.0 mL) were added **1a** (181.6 mg, 0.41 mmol) and a solution of PPh_3 (80.0 mg, 0.31 mmol) in THF (2.0 mL). After the mixture was stirred at 40 °C for 13 h, the solvent was removed under vacuum. The residue was washed with Et_2O (5.0 mL) and the filtrate was evaporated to give the solid, which was further washed with hexane (5.0 mL). Addition of hexane to the solution of this residue in CH_2Cl_2 afforded **5** (105.3 mg, 69%) as an orange solid: mp 169−171 °C. ^{1}H NMR (300 MHz) δ 0.21 (s, 6 H), 0.55 (s, J_{H-P} = 3.7 Hz, 2 H), 7.29 (ddm, J = 7.5, 5.8 Hz, 1 H), 7.34−7.42 (m, 9 H), 7.46 (dm, J = 7.5 Hz, 1 H), 7.65 (td, J = 7.7, 1.6 Hz, 1 H), 7.71−7.76 (m, 6 H), 9.63−9.65 (m, 1 H); ^{13}C NMR (100 MHz) δ 0.0, 15.8 (d, J_{C-P} = 3.8 Hz), 123.9 (d, J_{C-P} = 3.0 Hz), 128.1 (d, J_{C-P} = 10.6 Hz), 129.1 (d, J_{C-P} = 2.3 Hz), 130.2 (d, J_{C-P} = 2.3 Hz), 132.0 (d, J_{C-P} = 50.8 Hz), 134.5 (d, J_{C-P} = 11.4 Hz), 135.6, 152.4, 174.2 (d, J_{C-P} = 1.5 Hz); ^{31}P NMR (162 MHz) δ 37.2. X-ray data for **5**: $C_{26}H_{27}NSiPClPd$, M = 554.42, triclinic, space group $P\bar{1}$(No. 2), a = 10.2144(7) Å, b = 27.866-(2) Å, c = 9.4148(6) Å, V = 2600.5(3) Å^3, Z = 5, D_c = 1.77 g/cm^3, μ = 11.72 cm^{-1}. Intensity data were measured on a Rigaku RAXIS imaging plate area detector with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The data were collected at 23 ± 1 °C to a maximum 2θ value of 55.0°. A total of 9472 reflections were collected.

Two molecules were found in a unit cell. The structure was solved by direct methods and expanded by using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement on F was based on 8565 observed reflections ($I > 3.00\sigma(I)$) and 560 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of $R = 0.052$ ($R_w = 0.068$). The standard deviation of an observation of unit weight was 1.32. All calculations were performed by using the CrystalStructure crystallographic software package.

Procedure for the C−Si Oxidation of 2a (Scheme 3). To a mixture of KF (119 mg, 2.0 mmol) and $KHCO_3$ (207 mg, 2.1 mmol) in MeOH (2 mL) and THF (2 mL) were added **2a** (256 mg, 1.1 mmol) and 30% aqueous H_2O_2 (2.3 g, 20 mmol) and the reaction mixture was stirred at 50 °C for 12 h. After being cooled to room temperature, the reaction mixture was treated with H_2O (10 mL). The mixture was extracted with Et_2O (5 × 10 mL) and the combined organic phase was successively washed with 15% aqueous $Na_2S_2O_3$ (10 mL). Drying over $MgSO_4$ and removal of solvents under reduced pressure afforded crude benzyl alcohol. The yield of benzyl alcohol (**6a**) was 94% as judged by capillary GC analysis with *n*-pentadecane as an internal standard.

Procedure for the TBAF-Catalyzed Reaction of 2 with Carbonyl Compound (Scheme 3). To a solution of benzaldehyde (52.8 mg, 0.50 mmol) and tetrabutylammonium fluoride (0.025 mmol, 5 mol %, 1.0 M solution in THF) in THF (1.0 mL) was added **2a** (174.0 mg, 0.75 mmol) at room temperature. After the mixture was stirred for 4 h, 1 N aqueous HCl (2 mL) was added to the mixture. The mixture was extracted with Et_2O (5 × 2 mL) and the combined organic phase was dried over $MgSO_4$. Removal of solvents under reduced pressure and subsequent silica gel chromatography (hexane/EtOAc = 5/1) afforded 1,2-diphenylethanol (**7a**) (92.6 mg, 94%) as colorless solid.

1,2-Diphenylethanol (7a).[38] ^{1}H NMR (300 MHz) δ 2.08 (br s, 1 H), 3.00 (dd, J = 13.8, 8.1 Hz, 1 H), 3.07 (dd, J = 13.5, 5.1 Hz, 1 H), 4.90 (dd, J = 8.4, 5.4 Hz, 1 H), 7.20−7.38 (m, 10 H).

1,4-Diphenylbut-3-en-2-ol (7b).[39] This compound was obtained in 68% yield from **2a** (1.5 equiv) and *trans*-cinnamaldehyde (1.0 equiv) in the presence of TBAF (5 mol %). ^{1}H NMR (300 MHz) δ 1.64 (br s, 1 H), 2.89 (dd, J = 13.5, 7.8 Hz, 1 H), 2.99 (dd, J = 13.8, 5.1 Hz, 1 H), 4.54 (ddd, J = 12.0, 6.3, 1.2 Hz, 1 H), 6.29 (dd, J = 15.9, 6.3 Hz, 1 H), 6.61 (d, J = 16.2 Hz, 1 H), 7.22−7.40 (m, 10 H).

1,2-Diphenylpropan-2-ol (7c).[38] This compound was obtained in 70% yield from **2a** (1.5 equiv) and acetophenone (1.0 equiv) in the presence of TBAF (5 mol %). ^{1}H NMR (300 MHz) δ 1.57 (s, 3 H), 1.84 (br s, 1 H), 3.03 (d, J = 13.2 Hz, 1 H), 3.14 (d, J = 13.2 Hz, 1 H), 6.99 (dd, J = 6.0, 2.1 Hz, 2 H), 7.21−7.42 (m, 8 H).

4-(2-Hydroxy-2-phenyl)acetophenone (7d).[40] This compound was obtained in 54% yield from **2b** (1.5 equiv) and benzaldehyde (1.0 equiv) in the presence of TBAF (5 mol %). ^{1}H NMR (300 MHz) δ 2.08 (br s, 1 H), 2.58 (s, 3 H), 3.06 (dd, J = 13.5, 6.0 Hz, 1 H), 3.11 (dd, J = 13.5, 7.5 Hz, 1 H), 4.93 (dd, J = 7.2, 6.0 Hz, 1 H), 7.25 (m, 7 H), 7.87 (d, J = 8.1 Hz, 2 H).

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Supporting Information Available: Tables of crystallographic data for **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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