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# Efficient Preparation of Monohydrosilanes Using Palladium-Catalyzed Si–C Bond Formation

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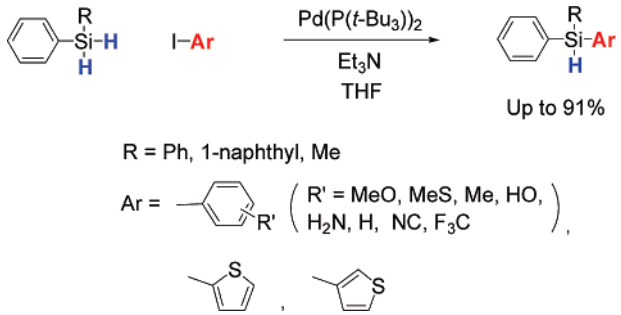
## ABSTRACT




**The arylation of dihydrosilanes with aryl iodides or heteroaryl iodides in the presence of a palladium catalyst provides the corresponding monohydrosilanes in good to high yield. Moderate to good yields are obtained even in the presence of a variety of reactive functional groups, such as –$NH_2$, –OH, or –CN, without their protection.**

The transition-metal-catalyzed cross-coupling reaction has become an important method for carbon−heteroatom bond formation.[1] In particular, there have been significant developments in the formation of carbon−silicon bonds due to the recent interest in organosilane compounds as intermediates for Hiyama coupling[2] and in advanced materials such as ultrahigh energy gap hosts in deep blue organic electrophosphorescent devices.[3] In particular, monohydrosilanes are extremely useful intermediates to construct novel organosilicon compounds. Although their preparation has been traditionally accomplished by the treatment of Grignard or organolithium reagents with dichlorosilanes followed by the treatment of $LiAlH_4$ (Scheme 1, Route A), this method is a multistep process and is available only for a limited number of substrates.[4] A recent strategy is the direct conversion of carbon−halogen bonds to carbon−silicon bonds with hydrosilanes in the presence of transition-metal catalysts.[5−7] During the course of our studies, we have developed a method for palladium- and rhodium-catalyzed silylation of

(1) For representative reviews, see: (a) Hartwig, J. F. *Pure Appl. Chem.* **1999**, *71*, 1417. (b) Beletskaya, I. P. *Pure Appl. Chem.* **2005**, *77*, 2021. (c) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359. (d) Denmark, S. E.; Sweis, R. F. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiely-VCH: Weinheim, 2004. (e) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley & Sons: Chichester, 2004. (f) Prim, D.; Campagne, J.-M.; Joseph, D.; Andrioletti, B. *Tetrahedron* **2002**, *58*, 2041.

(2) (a) Nakao, Y.; Sahoo, A. K.; Imanaka, H.; Yada, A.; Hiyama, T. *Pure Appl. Chem.* **2006**, *78*, 435. (b) Denmark, S. E.; Ober, M. H. *Aldrichim. Acta* **2003**, *36*, 75. (c) Hiyama, T.; Shirakawa, E. *Top. Curr. Chem.* **2002**, *219*, 61. (d) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317. (e) Hatanaka, Y.; Hiyama, T. *Synlett* **1991**, 845.

(3) (a) Ren, X.; Li, J.; Holmes, R.; Djurovich, P.; Forrest, S.; Thompson, M. *Chem. Mater.* **2004**, *16*, 4743. (b) Liu, X.-M.; He, C.; Huang, J.; Xu, J. *Chem. Mater.* **2005**, *17*, 434.

(4) Patai, S., Rappoport, Z., Eds. *The Chemistry of Organic Silicon Compounds*; John Wiley & Sons: New York, 1989.

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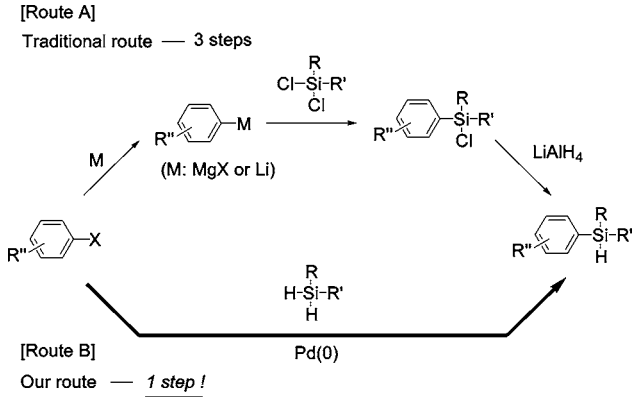
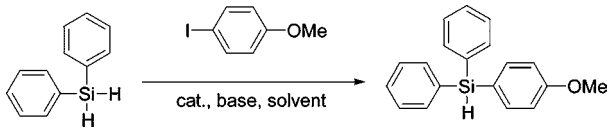
**Scheme 1.** Preparation of Monohydrosilanes




aryl halides with monohydrosilanes in the presence of $K_3PO_4$.[8] To expand the application of this method, we have developed a convenient and efficient approach (only one step!) to the preparation of monohydrosilanes (Scheme 1, Route B).[9]

Initially, the effects of catalysts, solvents, and bases in the monoarylation of diphenylsilane with 4-iodoanisole were examined. The results are shown in Table 1. Among the several transition-metal catalysts screened, $Pd(P(t\text{-}Bu_3))_2$ was a quite effective palladium source.[10] The reaction proceeded smoothly at 5 mol % catalyst loading. The phosphine ligand of palladium catalyst affected the silylation markedly; i.e., $Pd(PCy_3)_2$ and $Pd(PPh_3)_4$ did not show good catalytic activity. After screening bases, we recognized $Et_3N$ as being the most effective. The desired product was obtained in low yield without base. Among the solvents examined, the use of THF was essential for this silylation. Room temperature was found to be optimal for the reaction. The optimized conditions for the monoarylation were 4-iodoanisole (1.0 equiv), diphenylsilane (1.5 equiv), $Et_3N$ as base (1.5 equiv), and 5 mol % of $Pd(P(t\text{-}Bu)_3)_2$ in THF at room temperature under an argon atmosphere, which afforded the monoarylated product in 79% isolated yield.

**Table 1.** Optimization of the Preparation of 4-Methoxyphenyldiphenylsilane[a]

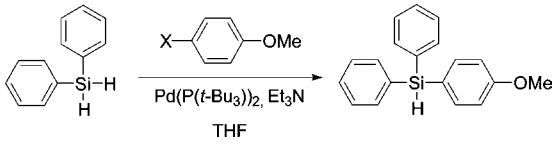



| entry | cat. | base | solvent | yield[b] (%) |
|---|---|---|---|---|
| **1** | **$Pd(P(t\text{-}Bu)_3)_2$** | **$Et_3N$** | **THF** | **79** |
| 2 | $Pd(PPh_3)_4$ | $Et_3N$ | THF | 35 |
| 3 | $Pd(PCy_3)_2$ | $Et_3N$ | THF | trace |
| 4 | $Pd(P(t\text{-}Bu)_3)_2$ | *c* | THF | *d* |
| 5 | $Pd(P(t\text{-}Bu)_3)_2$ | $i\text{-}Pr_2EtN$ | THF | 63 |
| 6 | $Pd(P(t\text{-}Bu)_3)_2$ | $K_3PO_4$ | THF | 23 |
| 7 | $Pd(P(t\text{-}Bu)_3)_2$ | $Na_2CO_3$ | THF | 5 |
| 8 | $Pd(P(t\text{-}Bu)_3)_2$ | $Et_3N$ | dioxane | 47 |
| 9 | $Pd(P(t\text{-}Bu_3)_2$ | $Et_3N$ | toluene | 43 |

[a] Reaction conditions: 4-iodoanisole (1.0 mmol), diphenylsilane (1.5 mmol), triethylamine (1.5 mmol), palladium catalyst (0.05 mmol), THF (1.0 mL) at rt for 2 d. [b] Isolated yield. [c] No base was added. [d] No appreciable reaction.

We next focused our attention on the scope of the leaving group on the aromatic ring. As outlined in Table 2, iodide, bromide, chloride, and triflate were all tested as leaving groups. Unfortunately, bromide, chloride, and triflate did not have enough reactivity; i.e., there was almost complete recovery of starting materials. In the case of aryl bromide, we then examined a treatment with an additional equal amount of tetraethylammonium iodide, and the yield of silylation slightly increased.

**Table 2.** Effect of Leaving Group[a]




| entry | X | additive | yield[b] (%) |
|---|---|---|---|
| 1 | I | *c* | 79 |
| 2 | Br | *c* | trace |
| 3 | Br | $Et_4NI$ | 14 |
| 4 | Cl | *c* | *d* |
| 5 | OTf | *c* | *d* |

[a] Reaction conditions: aryl halide or triflate (1.0 mmol), diphenylsilane (1.5 mmol), triethylamine (1.5 mmol), palladium catalyst (0.05 mmol), THF (1.0 mL), at rt for 2 days. [b] Isolated yield. [c] No additive. [d] Almost full recovery of starting material.

On the basis of these results, we examined the applicability of this catalytic system to other aryl iodides and dihydro-

(5) Hydrosilanes generally work as reducing reagents in the presence of palladium catalyst. For example, see: (a) Boukherroub, R.; Chatgilialoglu, C.; Manuel, G. *Organometallics* **1996**, *15*, 1508. (b) Fuwa, H.; Sasaki, M. *Org. Bio. Chem.* **2007**, *5*, 1849.

(6) For example, see: (a) Murata, M.; Ota, K.; Yamasaki, H.; Watanabe, S.; Masuda, Y. *Synlett* **2007**, 1387. (b) Murata, M.; Yamasaki, H.; Ueta, T.; Nagata, M.; Ishikura, M.; Watanabe, S.; Masuda, Y. *Tetrahedron* **2007**, *63*, 4087. (c) Murata, M.; Ohara, H.; Oiwa, R.; Watanabe, S.; Masuda, Y. *Synthesis* **2006**, 1771. (d) Hamze, A.; Provot, O.; Alami, M.; Brion, J.-D. *Org. Lett.* **2006**, *8*, 931. (e) Karshtedt, D.; Bell, A. T.; Tilley, T. D. *Organometallics* **2006**, *25*, 4471. (f) Denmark, S. E.; Kallemeyn, J. M. *Org. Lett.* **2003**, *5*, 3483. (g) Komuro, K.; Ishizaki, K.; Suzuki, H. *Touagousei-kenkyu-nenpo* **2003**, *6*, 24. (h) Gu, W.; Liu, S.; Silverman, R. B. *Org. Lett.* **2002**, *4*, 4171. (i) Murata, M.; Ishikura, M.; Nagata, M.; Watanabe, S.; Masuda, Y. *Org. Lett.* **2002**, *4*, 1843. (j) Manoso, A. S.; Deshong, P. J. *Org. Chem.* **2001**, *66*, 7455. (k) Murata, M.; Watanabe, S.; Masuda, Y. *Tetrahedron Lett.* **1999**, *40*, 9255. (l) Murata, M.; Suzuki, K.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **1997**, *62*, 8569.

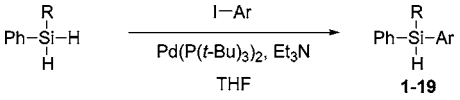
(7) Although the transition-metal-catalyzed hydrogenative coupling of Si−H bonds with aromatic C−H bonds has been reported, the reaction is a little problematic with regard to the control of selectivity due to the drastic conditions. For recent representative reports, see: (a) Tsukada, N.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 5022. (b) Ezbiansky, K.; Djurovich, P. I.; LaForest, M.; Sinning, D. J.; Zayes, R.; Berry, D. H. *Organometallics* **1998**, *17*, 1455.

(8) (a) Yamanoi, Y. *J. Org. Chem.* **2005**, *70*, 9607. (b) Yamanoi, Y.; Nishihara, H. *Tetrahedron Lett.* **2006**, *47*, 7157.

(9) Fujiwara et al. reported the selective preparation of monohydrosilanes by the reactions of dihydrosilanes with an equivalent amount of organolanthanide iodides. (a) Jin, W.-S.; Makioka, Y.; Kitamura, T.; Fujiwara, Y. *Chem. Commun.* **1999**, 955. (b) Makioka, Y.; Fujiwara, Y.; Kitamura, T. *J. Organomet. Chem.* **2000**, *611*, 509.

silanes. A variety of triorganosilanes were synthesized in a one-step process in good to high yields in the presence of $Pd(P(t\text{-}Bu)_3)_2$ with $Et_3N$ in THF at rt for 2 d.[11] The representative results are shown in Table 3. Substituents on

**Table 3.** Arylation of Dihydrosilanes Mediated by Palladium Catalyst



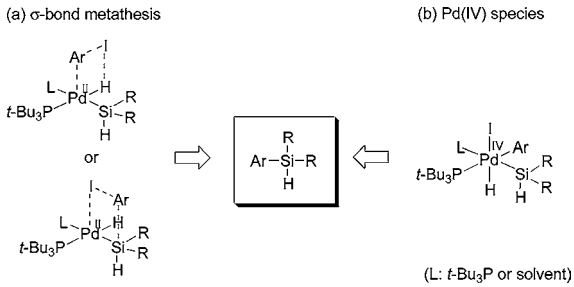

| entry | R | Ar | conditions[a] | product | yield[b] (%) |
|---|---|---|---|---|---|
| 1 | Ph | 4-$MeOC_6H_4$ | A | **1** | 79 |
| 2 | Ph | Ph | A | **2** | 63 |
| 3 | Ph | 2-$MeOC_6H_4$ | A | **3** | 78 |
| 4 | Ph | 4-$MeC_6H_4$ | A | **4** | 62 |
| 5 | Ph | 3-$MeC_6H_4$ | A | **5** | 63 |
| 6 | Ph | 3-$H_2NC_6H_4$ | A | **6** | 66 |
| 7 | Ph | 1-naphthyl | A | **7** | 60 |
| 8 | Ph | 2-$C_4H_4S$ | A | **8** | 66 |
| 9 | Ph | 3-$C_4H_4S$ | A | **9** | 77 |
| 10 | Ph | 4-$F_3CC_6H_4$ | A | **10** | 67 |
| 11 | Ph | 2,6-$Me_2C_6H_3$ | A | – | *c* |
| 12 | 1-naphthyl | 4-$MeOC_6H_4$ | A | **11** | 91 |
| 13 | 1-naphthyl | 2-$MeOC_6H_4$ | A | **12** | 79 |
| 14 | 1-naphthyl | 2,4-$Me_2C_6H_3$ | A | **13** | 84 |
| 15 | 1-naphthyl | 4-$HOC_6H_4$ | B | **14** | 46 |
| 16 | 1-naphthyl | 4-$NCC_6H_4$ | C | **15** | 64 |
| 17 | 1-naphthyl | 2-$C_4H_4S$ | A | **16** | 60 |
| 18 | 1-naphthyl | 4-$F_3CC_6H_4$ | A | **17** | 76 |
| 19 | Me | 2-$MeOC_6H_4$ | A | **18** | 65 |
| 20 | Me | 2-$MeC_6H_4$ | A | **19** | 70 |

[a] Reaction conditions. A: aryl iodide (1.0 mmol), dihydrosilane (1.5 mmol), triethylamine (1.5 mmol), $Pd(P(t\text{-}Bu)_3)_2$ (0.05 mmol), THF (1.0 mL), at rt for 2 d. B: aryl iodide (1.0 mmol), dihydrosilane (3.0 mmol), triethylamine (3.0 mmol), $Pd(P(t\text{-}Bu)_3)_2$ (0.05 mmol), THF (1.0 mL), at rt for 2 d. C: aryl iodide (1.0 mmol), dihydrosilane (3.0 mmol), triethylamine (3.0 mmol), $Pd(P(t\text{-}Bu)_3)_2$ (0.05 mmol), THF (1.0 mL), at 0 °C for 5 d. [b] Isolated yield. [c] Not obtained.

the aromatic ring little influenced the yield of silylated products. This arylation has proved to be compatible with reactive functional groups such as the free amine ($-NH_2$), phenolic moiety (−OH), or nitrile group (−CN) (entries 6, 15, and 16) on the aromatic ring. In contrast, the traditional methods through Grignard or organolithium reagents require protection of the functional group.[4] In addition, ortho-substituted aryl halides gave corresponding arylsilanes in good yields (entries 3, 7, 13, 14, 19, and 20). However, it was difficult to couple 2,6-disubstituted aryl iodide with diphenylsilane because of the large steric effect (entry 11). Furthermore, heteroaromatic iodides were also coupled with dihydrosilanes without any difficulty (entries 8, 9, and 17). As a whole, the silylated products were contaminated with a small amount of the reduced byproducts in every case. However, their separation was very easy. Accordingly, the present reaction provides a simple and widely available procedure for the preparation of monohydrosilane.[12,13]

Although the mechanistic details of the reaction are not yet clear, we envisaged the pathway for Si−C bond formation as depicted in Scheme 2. Initially, dihydrosilanes would

**Scheme 2.** Reaction Mechanism




add oxidatively to Pd(0) to generate the $H-Pd^{II}-SiHR_2$ species. Then, a pathway through $\sigma$-bond metathesis[14,15] between the Pd(II) species and aryl iodide would lead to the arylsilanes (Scheme 2(a)). However, we cannot completely rule out a pathway through further oxidative addition of Ar−I

(10) For representative studies on the use of $P(t\text{-}Bu)_3$ in palladium-catalyzed coupling reactions, see: (a) Nishiyama, M.; Yamamoto, T.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 617. (b) Yamamoto, T.; Nishiyama, M.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 2367. (c) Watanabe, M.; Nishiyama, M.; Koie, Y. *Tetrahedron Lett.* **1999**, *40*, 8837. (d) Watanabe, M.; Nishiyama, M.; Yamamoto, T.; Koie, Y. *Tetrahedron Lett.* **2000**, *41*, 481. (e) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **1998**, *37*, 3387. (f) Shaughnessy, K. H.; Kim, P.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 2123. (g) Littke, A. F.; Fu, G. C. *J. Org. Chem.* **1999**, *64*, 10. (h) Netherton, M. R.; Fu, G. C. *Org. Lett.* **2001**, *3*, 4295. (i) Hundertmark, T.; Littke, A. F.; Buchwald, S. L.; Fu, G. C. *Org. Lett.* **2000**, *2*, 1729. (j) Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 2719. (k) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020. (l) Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 6989. (m) Fu, G. C. *J. Org. Chem.* **2004**, *69*, 3245.

(11) **Typical Experimental Procedure for a Palladium-Catalyzed Monoarylation Reaction.** The general procedure for palladium-catalyzed silylation is illustrated by the synthesis of (4-methoxyphenyl)diphenylsilane. To a solution of $Pd(P(t\text{-}Bu)_3)_2$ (25 mg 0.049 mmol) in THF (1.0 mL) were added diphenylsilane (0.32 mL, 1.5 mmol), 4-iodoanisole (234 mg 1.0 mmol), and triethylamine (0.40 mL, 3.0 mmol). After being stirred for 2 d at room temperature, the reaction mixture was quenched with water, extracted with $CH_2Cl_2$ three times, and dried over $Na_2SO_4$. The solvent was evaporated under reduced pressure, and column chromatography on slica gel (eluent: hexane/EtOAc = 10/1) afforded (4-methoxyphenyl)-diphenylsilane (229 mg, 79%).

(12) In all cases, reduced products (arenes) were observed as side products, and no double- arylated products were observed by GC−MS measurement of the reaction mixture. However, double-arylated products were obtained in the presence of an excess amount of aryl iodides for a prolonged reaction time. For the preparation of double- arylated products, see ref 13.

(13) **Typical Experimental Procedure for Palladium-Catalyzed Double-Arylation Reactions.** The procedure for palladium-catalyzed silylation is illustrated by the synthesis of di(4-methoxyphenyl)diphenyl-silane. To a solution of $Pd(P(t\text{-}Bu)_3)_2$ (12.8 mg, 0.025 mmol) in THF (1.0 mL) were added diphenylsilane (94 $\mu$L, 0.5 mmol), aryl iodide (1.5 mmol), and triethylamine (0.2 mL, 1.5 mmol). After being stirred for 4 d at room temperature, the reaction mixture was quenched with water, extracted with $CH_2Cl_2$ three times, and dried over $Na_2SO_4$. The solvent was evaporated under reduced pressure, and fractionated column chromatography was carried out on silica gel to afford the double-arylated product: tetra-phenylsilane (**20**), 49%; di(4-methoxyphenyl)diphenylsilane (**21**), 72%; and di(4-methylthiophenyl)diphenylsilane (**22**), 58%.

(14) Kunai and his co-workers reported that the $PdCl_2$-catalyzed reaction of alkyl iodides with $Et_2SiH_2$ afforded $REt_2SiI$ and $Et_2SiI_2$ through $\sigma$-bond metathesis. Kunai, A.; Sakurai, T.; Toyoda, E.; Ishikawa, M.; Yamamoto, Y. *Organometallics* **1994**, *13*, 3233.

(15) For a review, see: Perutz, R. N.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 2578.

to form a Pd(IV) intermediate (Scheme 2(b)).[16] The present experimental studies cannot ascertain which mechanism is actually taking place.

In summary, an inexpensive and highly efficient catalytic system for the preparation of monohydrosilanes has been developed. Compared with traditional methods, several interesting features are apparent on the basis of the present results, including the following: (1) The catalytic system is efficient and general for a variety of aryl iodides. (2) Several functional groups, including amino, hydroxy, or cyano groups, could be well-tolerated. (3) The inexpensive catalytic system emerged as an attractive alternative to the Grignard or organolithium method. Further efforts to reveal the reaction mechanism and to extend the application of the system are underway in our laboratory.

(16) For reviews of organopalladium(IV) chemistry, see: (a) Canty, A. J. *Acc. Chem. Res*. **1992**, *25*, 83. (b) Canty, A. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 9. (c) Canty, A. J. Palladium Complexes Containing Pd(I), Pd(III), or Pd(IV). In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E.-i., Ed.; Wiley-Interscience: New York, 2002; pp 189−211.

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**Supporting Information Available:** General information, compound characterization data, and copies of the $^{1}H$ and $^{13}C$ NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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