Received: October 2, 2013 | Accepted: October 18, 2013 | Web Released: October 26, 2013 CL-130919

Synthesis of HOMSi Reagents by Pd/Cu-Catalyzed Silylation of Bromoarenes with Disilanes

Yasunori Minami,*[1,2] Kenta Shimizu,[3] Chisato Tsuruoka,[3] Takeshi Komiyama,[3] and Tamejiro Hiyama*[1,2]
[1]*Research and Development Initiative, Chuo University, Kasuga, Bunkyo-ku, Tokyo 112-8551*
[2]*JST, ACT-C, Kasuga, Bunkyo-ku, Tokyo 112-8551*
[3]*Faculty of Science and Engineering, Chuo University, Kasuga, Bunkyo-ku, Tokyo 112-8551*

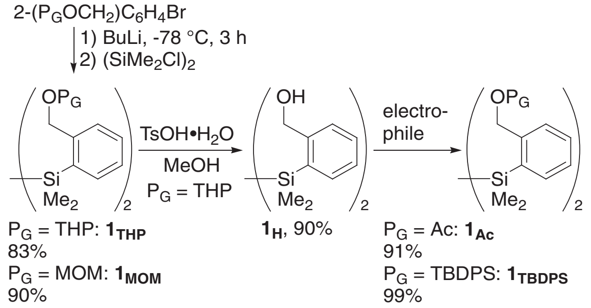
(E-mail: yminami@kc.chuo-u.ac.jp)

Silylation of aryl bromides with disilanes of type $\{[2\text{-}(P_GOCH_2)C_6H_4]Me_2Si\}_2$ (P_G: protecting group) successfully takes place in the presence of a Pd/Ruphos or Davephos/CuI catalytic system to afford HOMSi reagents containing various functional groups in good yields. BisHOMSi reagents were also prepared directly from the corresponding arylene dibromides.

Organosilicon compounds are selective, stable, and thus, useful reagents for chemoselective organic synthesis. Of the many functional tolerant transformations, metal-catalyzed cross-coupling with organic halides are representative.[1] Accordingly, silicon-based cross-coupling reaction is gaining prominence among various cross-coupling methodologies. In particular, the tetraorganosilicon-type coupling reagents organo-[2-(hydroxymethyl)phenyl]dimethylsilanes (R-HOMSi) are unique for easy handling and facile recovery and reuse of the Si moiety; these reagents are now commercially available worldwide.[2,3] Ar-HOMSi reagents have high potential for the synthesis of functionalized oligoarenes and polyarenes. A typical preparative method for Ar-HOMSi reagents is the reaction of organometallic reagents with a cyclic silyl ether, $1,2\text{-}(SiMe_2OCH_2)C_6H_4$. However, functionalized Ar-HOMSi reagents are less accessible by this method because of the insufficient chemoselective transformation. To overcome this disadvantage, transition-metal-catalyzed silylation of organic halides with disilanes[4–6] or hydrosilanes[7] appears to be highly promising for the synthesis of functionalized organosilicon reagents. In this respect, preparation of Ar-HOMSi reagents by the silylation of bromoarenes with hydrosilanes is attractive, as reported by Kondo et al. However, yields remain only moderate and the scope is limited.[7k] Because disilanes are also applicable to such silylation, we focused on the use of disilanes for the silylation of aryl halides and herein report a new synthesis of Ar-HOMSi reagents by the palladium/copper-catalyzed silylation of organic halides.

Protected 2-bromophenylmethanol was lithiated with butyllithium; the resulting aryllithium was allowed to react with 1,2-dichlorotetramethyldisilane to afford protected disilanes (Scheme 1). Thus, THP-protected disilane **1**$_{\mathbf{THP}}$ was isolated in 83% yield. In a similar way, MOM-protected disilane **1**$_{\mathbf{MOM}}$ was prepared in 90% yield. Other protected disilanes having acetyl (**1**$_{\mathbf{Ac}}$) and TBDPS (**1**$_{\mathbf{TBDPS}}$) groups were prepared by the deprotection of **1**$_{\mathbf{THP}}$, followed by the protection of the resulting **1**$_{\mathbf{H}}$ by acetylation or silylation to afford **1**$_{\mathbf{Ac}}$ and **1**$_{\mathbf{TBDPS}}$ in 91% and quantitative yields, respectively.

We first tested the reported conditions[4f–4h,4j] for the silylation of *p*-bromotoluene (**2a**) using **1**$_{\mathbf{THP}}$ in the presence of a base without any success: no trace or only small amounts of the desired product, protected *p*-tolyl-HOMSi (**3a**), was produced (See Supporting Information).[8] Thus, we next examined many other activation protocols for **1** as the silylation reagent and found the catalyst system recorded by Hosomi[9a] to be informative: in situ generation of silylcopper reagents by the reaction of disilanes with Cu(OTf).[9] On the basis of this report, we planned the generation of protected HOMSi copper reagent by treatment of disilyl reagents **1** with Cu(I) for the silylation of organic halides.[10] Of the many catalysts and additives examined, we found that the reaction system consisting of $[Pd(allyl)Cl]_2$, Ruphos (2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl), CuI, K_2CO_3, and THF/DMF (3:1) as a solvent showed catalytic activity to afford **3a** in 34% (NMR) yield together with siloxane **4** in 92% yield (Table 1, Run 1). Other copper salts such as CuBr, $CuBr{\cdot}SMe_2$, and CuCl were less effective. K_2CO_3 was proved to be the best; other bases such as Na_2CO_3, Cs_2CO_3, and K_3PO_4 resulted in lower yields of **3a**. In the absence of CuI, palladium, or K_2CO_3, formation of **3a** was not observed, though **4** was generated, maybe via an attack of the carboxylate anion or iodonium ion from CuI to **1**$_{\mathbf{THP}}$ (Runs 2–4). These results indicate that the silyl copper reagent is formed as an active silyl nucleophile, possibly by the reaction of **1**$_{\mathbf{THP}}$ with CuI in the presence of K_2CO_3. To enhance the efficiency, various solvents were further examined and the reaction in dioxane/NMP (4:1) at 100 °C afforded **3a** in 80% yield (Run 5). In this solvent without CuI, **3a** was obtained in 52% yield (Run 6). These results suggest that the highly polar solvents definitely increase the silylation efficiency, as is evidenced by the couse of H_2O that further increased the yield and shortened the reaction time (Run 7). Finally, the yield was improved to 87% in the presence H_2O (Run 8).

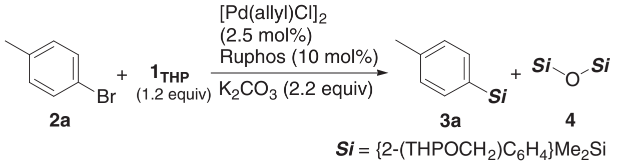


Scheme 1. Preparation of disilanes **1**.

Deprotection of **3a** by TsOH in methanol readily afforded the cross-coupling active *p*-tolyl-HOMSi reagent **5**.

The scope and limitations of the synthetic method under the optimized conditions are summarized in Table 2. Protected disilanes **1**$_{\mathbf{MOM}}$, **1**$_{\mathbf{Ac}}$, and **1**$_{\mathbf{TBDPS}}$ reacted with **2a** in a similar manner to afford products **6a**, **7a**, and **8a** in moderate to high

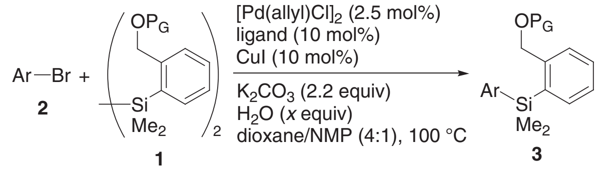
Table 1. Reaction of **2a** with $\mathbf{1_{THP}}$[a]

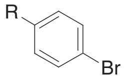
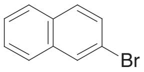
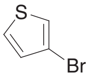


Run	Additive	Solvent	Temp /°C	Time /h	Yield/%[b]	
					3a	**4**[c]
1	CuI (10 mol %)	THF/DMF[d]	80	24	34	92
2	—	THF/DMF[d]	80	24	0	71
3[e]	CuI (10 mol %)	THF/DMF[d]	80	24	0	72
4[f]	CuI (10 mol %)	THF/DMF[d]	80	24	0	13
5	CuI (10 mol %)	dioxane/NMP[g]	100	24	80	85
6	—	dioxane/NMP[g]	100	24	52	76
7	CuI (10 mol %) H_2O (4 equiv)	dioxane/NMP[g]	100	2	83	11
8	CuI (10 mol %) H_2O (4 equiv)	dioxane/NMP[g]	100	24	87 (73)[h]	77

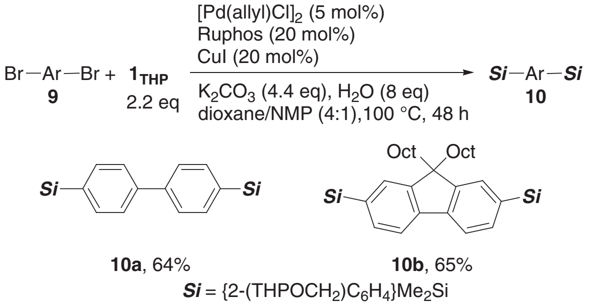
[a]Unless otherwise noted, **2**, $\mathbf{1_{THP}}$ (1.2 equiv), $[Pd(allyl)Cl]_2$ (2.5 mol %), ligand (10 mol %), CuI (10 mol %), K_2CO_3 (2.2 equiv), and solvent (0.36 M). [b]NMR yield. [c]Yields based on $\mathbf{1_{THP}}$. [d]3:1. [e]Without $[Pd(allyl)Cl]_2$. [f]Without K_2CO_3. [g]4:1. [h]Isolated yield.

Table 2. Silylation of organobromides **2** using disilane **1**[a]



Run	1	2	Ligand	H_2O (*x* equiv)	Time /h	Product /%[b]
1	$\mathbf{1_{MOM}}$	**2a**	L1	4	24	**6a**, 80%
2	$\mathbf{1_{Ac}}$	**2a**	L1	4	24	**7a**, 60%
3	$\mathbf{1_{TBDPS}}$	**2a**	L1	4	24	**8a**, 54%
						
4	$\mathbf{1_{THP}}$	**2b**: R = OMe	L1	4	24	**3b**, 75%
5	$\mathbf{1_{THP}}$	**2c**: R = NH(Boc)	L1	4	13	**3c**, 74%
6	$\mathbf{1_{THP}}$	**2d**: R = NPh_2	L1	4	16	**3d**, 67%
7	$\mathbf{1_{THP}}$	**2e**: R = 3,5-xylyl	L1	0	24	**3e**, 63%
8	$\mathbf{1_{THP}}$	**2f**: R = H	L2	4	24	**3f**, 64%
9[c]	$\mathbf{1_{THP}}$	**2g**: R = F	L2	0	24	**3g**, 60%
10[c]	$\mathbf{1_{THP}}$	**2h**: R = Cl	L2	0	16	**3h**, 63%
11	$\mathbf{1_{THP}}$	**2i**: R = Ph	L2	0	24	**3i**, 70%
12	$\mathbf{1_{MOM}}$	**2j**: R = Ac	L2	0	48	**6j**, 35%
13[d]	$\mathbf{1_{THP}}$	**2k**: R = CN	L2	1	31	**3k**, 26%
14[d]	$\mathbf{1_{THP}}$	**2l**: R = CF_3	L2	1	23	**3l**, 63%
15	$\mathbf{1_{THP}}$	**2m**: R = CHO	L2	0	48	**3m**, 27%
16	$\mathbf{1_{THP}}$	 **2n**	L2	0	24	**3n**, 70%
17	$\mathbf{1_{THP}}$	 **2o**	L1	4	24	**3o**, 42%

[a]Unless otherwise noted, **2** (0.5 mmol), **1** (0.6 mmol), $[Pd(allyl)Cl]_2$ (0.0125 mmol), ligand (0.05 mmol), CuI (0.05 mmol), K_2CO_3 (1.1 mmol), and 1,4-dioxane/NMP (4:1, 1.4 mL) were heated at 100 °C. [b]Isolated yield. [c]120 °C. [d]80 °C. L1 = Ruphos. L2 = Davephos.



Scheme 2.

yields (Runs 1–3). Various organic bromides were next subjected to the reaction with $\mathbf{1_{THP}}$ and $\mathbf{1_{MOM}}$. Electron-donating groups such as *p*-MeO, *p*-NHBoc, and *p*-Ph_2N did not hamper the reaction in the presence of Ruphos, and the corresponding protected HOMSi reagents **3b**–**3d** were isolated in moderate to good yields (Runs 4–6). In the case of 3,5-xylyl bromide (**2e**), H_2O did not enhance the reactivity: **3e** was isolated in 63% yield in the absence of H_2O (Run 7). In contrast, electron-neutral or electron-deficient aryl bromides afforded the corresponding protected Ar-HOMSi in low yields. As pointed out in many reports on the silylation of haloarenes with hydrosilanes or disilanes,[4f,4j,7d,7e] we further screened ligands for silylation using these bromides and found that Davephos, 2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl, led to the improvement of the catalytic activity. Thus, with Davephos, bromobenzene (**2f**) was converted to protected Ph-HOMSi **3f** in 64% yield (Run 8). Electron-deficient aryl bromides preferred the reaction in the absence or 1 equiv amount of H_2O (Runs 9–15). The reaction of 1-bromo-4-fluorobenzene (**2g**) afforded protected 4-F-C_6H_4-HOMSi reagent **3g** in 60% yield (Run 9). Other electron-deficient groups such as chloro, phenyl, acetyl, cyano, trifluoromethyl, and formyl tolerated well the silylation with $\mathbf{1_{THP}}$ and $\mathbf{1_{MOM}}$ to afford the corresponding protected HOMSi reagents **3h**–**3i**, **6j**, and **3k**–**3m** in 26–70% yields (Runs 10–15). The reaction of 2-bromonaphthalene (**2n**) afforded **3n** in 70% yield (Run 16). 3-Bromothiophene (**2o**) was silylated with $\mathbf{1_{THP}}$ in the presence of Ruphos and 4 equiv of H_2O to afford protected 3-thienyl-HOMSi reagent **3o** in 42% yield (Run 17).

This silylation can be applied to the synthesis of protected bis-HOMSi reagents **10** by the reaction of dibromoarenes **9** (Scheme 2). For example, 4,4′-dibromobiphenyl (**9a**) was bissilylated by 2.2 equiv of $\mathbf{1_{THP}}$ under the optimized conditions using Ruphos to afford protected 4,4′-biphenylylene-bisHOMSi reagent **10a** in 64% yield. Similarly, 2,7-dibromo-9,9′-dioctyl-9*H*-fluorene (**9b**) was double silylated to form the corresponding products **10b** in 65% yield.

We propose the reaction mechanism illustrated in Figure 1. Oxidative addition of aryl bromide **2** to palladium(0) complex forms an Ar–Pd–Br complex, which transmetalates to the silyl copper(I) reagent derived from the reaction of disilane **1** with

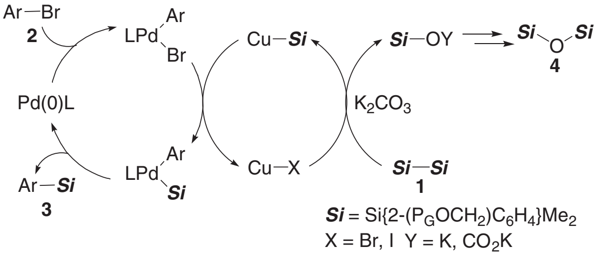


Figure 1. Proposed reaction mechanism.

Cu–X and K$_2$CO$_3$ to afford Ar–Pd–***Si*** complex with the generation of an oxysilane (***Si***–OY) and Cu–X. Finally, reductive elimination of Ar–Pd–***Si*** complex produces protected HOMSi reagents **3** and regenerates palladium(0) to complete the catalytic cycle. The coproduced oxysilane appears to be readily converted to siloxane **4**.[11] The additive H$_2$O may be attributed to enhancement in the solubility of K$_2$CO$_3$ and thus promote the reactivity of **1** toward Cu(I) and K$_2$CO$_3$.

In conclusion, we have demonstrated that the silylation of aryl bromides with disilanes is a powerful tool for the preparation of aryl-HOMSi reagents. This method allows us to synthesize variously functionalized aryl-HOMSi reagents useful for the C–C bond-forming cross-coupling with aryl bromides after deprotection. Furthermore, bisHOMSi reagents also are readily prepared and conveniently used for polyarylene synthesis.

This work has been supported financially by a Grant-in-Aids for Scientific Research (S) (No. 21225005 to T.H.) and Young Scientists (B) (No. 25870747 to Y.M.) from JSPS.

This paper is dedicated to Prof. Irina Beletskaya for her contribution to organometallic chemistry.

References and Notes

1 Reviews: a) T. Hiyama, in *Metal-Catalyzed Cross-Coupling Reactions*, ed. by A. de Meijere, F. Diederich, Willey-VCH, Weinheim, **1998**, Chap. 10, pp. 421–454. doi:10.1002/9783527612222.ch10. b) T. Hiyama, E. Shirakawa, in *Cross-Coupling Reactions: A Practical Guide* in *Topics in Current Chemistry*, ed. by N. Miyaura, Springer, **2002**, Vol. 219, pp. 61–85. doi:10.1007/3-540-45313-X_3. c) S. E. Denmark, R. F. Sweis, in *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed., ed. by A. de Meijere, F. Diederich, Willey-VCH, Weinheim, **2004**, Chap. 4, pp. 163–216. doi:10.1002/9783527619535.ch4. d) J. Tsuji, *Palladium Reagents and Catalysts: New Perspectives for the 21st Century*, Wiley, Chichester, **2004**, p. 338. doi:10.1002/0470021209.ch3. e) C. J. Handy, A. S. Manoso, W. T. McElroy, W. M. Seganish, P. DeShong, *Tetrahedron* **2005**, *61*, 12201. f) Y. Nakao, T. Hiyama, in *Pharmaceutical Process Chemistry*, ed. by T. Shioiri, K. Izawa, T. Konoike, Willey-VCH, Weinheim, **2011**, Chap. 5, p. 101–126. doi:10.1002/9783527633678.ch5. g) Y. Nakao, T. Hiyama, *Chem. Soc. Rev.* **2011**, *40*, 4893. h) W.-T. T. Chang, R. C. Smith, C. S. Regens, A. D. Bailey, N. S. Werner, S. E. Denmark, in *Cross-Coupling with Organosilicon Compounds* in *Organic Reactions*, ed. by S. E. Denmark, Wiley-VCH, New Jersey, **2011**, Vol. 75, p. 213–746. doi:10.1002/0471264180.or075.03.

2 a) Y. Nakao, H. Imanaka, A. K. Sahoo, A. Yada, T. Hiyama, *J. Am. Chem. Soc.* **2005**, *127*, 6952. b) Y. Nakao, A. K. Sahoo, A. Yada, J. Chen, T. Hiyama, *Sci. Technol. Adv. Mater.* **2006**, *7*, 536. c) Y. Nakao, S. Ebata, J. Chen, H. Imanaka, T. Hiyama, *Chem. Lett.* **2007**, *36*, 606. d) Y. Nakao, J. Chen, H. Imanaka, T. Hiyama, Y. Ichikawa, W.-L. Duan, R. Shintani, T. Hayashi, *J. Am. Chem. Soc.* **2007**, *129*, 9137. e) Y. Nakao, J. Chen, M. Tanaka, T. Hiyama, *J. Am. Chem. Soc.* **2007**, *129*, 11694. f) Y. Nakao, M. Takeda, J. Chen, T. Hiyama, Y. Ichikawa, R. Shintani, T. Hayashi, *Chem. Lett.* **2008**, *37*, 290. g) J. Chen, M. Tanaka, A. K. Sahoo, M. Takeda, A. Yada, Y. Nakao, T. Hiyama, *Bull. Chem. Soc. Jpn.* **2010**, *83*, 554. h) S. Tang, M. Takeda, Y. Nakao, T. Hiyama, *Chem. Commun.* **2011**, *47*, 307. i) Y. Nakao, T. Hiyama, *J. Synth. Org. Chem., Jpn.* **2011**, *69*, 1221. j) K. Shimizu, Y. Minami, Y. Nakao, K.-i. Ohya, H. Ikehira, T. Hiyama, *Chem. Lett.* **2013**, *42*, 45.

3 a) N. Saito, T. Yamazaki, Y. Sato, *Tetrahedron Lett.* **2008**, *49*, 5073. b) S. J. Shirbin, B. A. Boughton, S. C. Zammit, S. D. Zanatta, S. M. Marcuccio, C. A. Hutton, S. J. Williams, *Tetrahedron Lett.* **2010**, *51*, 2971. c) S. M. Marcuccio, R. Epa, M. Moslmani, A. B. Hughes, *Tetrahedron Lett.* **2011**, *52*, 7178. d) P. F. Hudrlik, A. M. Hudrlik, Y. A. Jeilani, *Tetrahedron* **2011**, *67*, 10089. e) D. A. Rooke, E. M. Ferreira, *Org. Lett.* **2012**, *14*, 3328. f) J. Bergueiro, J. Montenegro, F. Cambeiro, C. Saá, S. López, *Chem.—Eur. J.* **2012**, *18*, 4401. g) A. B. Smith, III, A. T. Hoye, D. Martinez-Solorio, W.-S. Kim, R. Tong, *J. Am. Chem. Soc.* **2012**, *134*, 4533. h) Y. Miki, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2013**, *15*, 172. i) Z. Wang, S. Chang, *Org. Lett.* **2013**, *15*, 1990. j) D. Martinez-Solorio, A. T. Hoye, M. H. Nguyen, A. B. Smith, III, *Org. Lett.* **2013**, *15*, 2454. k) M. H. Nguyen, A. B. Smith, III, *Org. Lett.* **2013**, *15*, 4258. l) S. Tang, S.-H. Li, W.-b. Yan, *Tetrahedron Lett.* **2012**, *53*, 6743.

4 a) H. Matsumoto, S. Nagashima, K. Yoshihiro, Y. Nagai, *J. Organomet. Chem.* **1975**, *85*, C1. b) D. Azarian, S. S. Dua, C. Eaborn, D. R. M. Walton, *J. Organomet. Chem.* **1976**, *117*, C55. c) H. Matsumoto, K. Yoshihiro, S. Nagashima, H. Watanabe, Y. Nagai, *J. Organomet. Chem.* **1977**, *128*, 409. d) C. Eaborn, R. W. Griffiths, A. Pidcock, *J. Organomet. Chem.* **1982**, *225*, 331. e) Y. Hatanaka, T. Hiyama, *Tetrahedron Lett.* **1987**, *28*, 4715. f) L. J. Gooßen, A.-R. S. Ferwanah, *Synlett* **2000**, 1801. g) E. Shirakawa, T. Kurahashi, H. Yoshida, T. Hiyama, *Chem. Commun.* **2000**, 1895. h) S. E. Denmark, J. M. Kallemeyn, *Org. Lett.* **2003**, *5*, 3483. i) T. Iwasawa, T. Komano, A. Tajima, M. Tokunaga, Y. Obora, T. Fujihara, Y. Tsuji, *Organometallics* **2006**, *25*, 4665. j) E. McNeill, T. E. Barder, S. L. Buchwald, *Org. Lett.* **2007**, *9*, 3785.

5 a) A. Ricci, A. Degl'Innocenti, S. Chimichi, M. Fiorenza, G. Rossini, H. J. Bestmann, *J. Org. Chem.* **1985**, *50*, 130. b) K. Yamamoto, A. Hayashi, S. Suzuki, J. Tsuji, *Organometallics* **1987**, *6*, 974. c) J. D. Rich, *J. Am. Chem. Soc.* **1989**, *111*, 5886. d) T. Kashiwabara, M. Tanaka, *Organometallics* **2006**, *25*, 4648.

6 X.-F. Wu, H. Neumann, M. Beller, *Tetrahedron Lett.* **2012**, *53*, 582.

7 a) M. Murata, K. Suzuki, S. Watanabe, Y. Masuda, *J. Org. Chem.* **1997**, *62*, 8569. b) A. S. Manoso, P. DeShong, *J. Org. Chem.* **2001**, *66*, 7449. c) M. Murata, M. Ishikura, M. Nagata, S. Watanabe, Y. Masuda, *Org. Lett.* **2002**, *4*, 1843. d) Y. Yamanoi, *J. Org. Chem.* **2005**, *70*, 9607. e) A. Hamze, O. Provot, M. Alami, J.-D. Brion, *Org. Lett.* **2006**, *8*, 931. f) M. Murata, H. Ohara, R. Oiwa, S. Watanabe, Y. Masuda, *Synthesis* **2006**, 1771. g) D. Karshtedt, A. T. Bell, T. D. Tilley, *Organometallics* **2006**, *25*, 4471. h) Y. Yamanoi, H. Nishihara, *Tetrahedron Lett.* **2006**, *47*, 7157. i) M. Murata, H. Yamasaki, T. Ueta, M. Nagata, M. Ishikura, S. Watanabe, Y. Masuda, *Tetrahedron* **2007**, *63*, 4087. j) Y. Yamanoi, T. Taira, J.-i. Sato, I. Nakamula, H. Nishihara, *Org. Lett.* **2007**, *9*, 4543. k) M. Iizuka, Y. Kondo, *Eur. J. Org. Chem.* **2008**, 1161. l) Y. Yamanoi, H. Nishihara, *J. Org. Chem.* **2008**, *73*, 6671. m) N. Iranpoor, H. Firouzabadi, R. Azadi, *J. Organomet. Chem.* **2010**, *695*, 887. n) A. Lesbani, H. Kondo, J.-i. Sato, Y. Yamanoi, H. Nishihara, *Chem. Commun.* **2010**, *46*, 7784. o) A. Lesbani, H. Kondo, Y. Yabusaki, M. Nakai, Y. Yamanoi, H. Nishihara, *Chem.—Eur. J.* **2010**, *16*, 13519. p) C. Huang, N. Chernyak, A. S. Dudnik, V. Gevorgyan, *Adv. Synth. Catal.* **2011**, *353*, 1285. q) Y. Kurihara, M. Nishikawa, Y. Yamanoi, H. Nishihara, *Chem. Commun.* **2012**, *48*, 11564. r) H. Inubushi, H. Kondo, A. Lesbani, M. Miyachi, Y. Yamanoi, H. Nishihara, *Chem. Commun.* **2013**, *49*, 134.

8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

9 a) H. Ito, T. Ishizuka, J.-i. Tateiwa, M. Sonoda, A. Hosomi, *J. Am. Chem. Soc.* **1998**, *120*, 11196. b) C. T. Clark, J. F. Lake, K. A. Scheidt, *J. Am. Chem. Soc.* **2004**, *126*, 84.

10 a) F. Geng, R. E. Maleczka, Jr., *Tetrahedron Lett.* **1999**, *40*, 3113. b) H. Azuma, K. Okano, H. Tokuyama, *Chem. Lett.* **2011**, *40*, 959.

11 R. Minkwitz, S. Schneider, *Z. Naturforsch. B* **1998**, *53*, 849.