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# Synthesis of Functionalized Benzylsilanes from Arylzinc Compounds and (Iodomethyl)trimethylsilane by Means of a Novel Rh Catalysis

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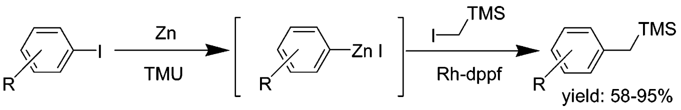

The catalytic activity of a Rh complex in cross-coupling between ArZnI and $TMSCH_2I$ was examined in which the Rh complex, generated in situ from $[RhCl(1,5\text{-cyclooctadiene})]_2$ and 1,1′-bis(diphenylphosphino)-ferrocene, exhibited excellent catalytic activity for the production of various functionalized benzylsilanes in good yields. From $^{31}P$ NMR studies of various solutions containing several of the reaction components, confirmation of the rapid and quantitative transfer of aryl groups from ArZnI to the Rh complex to form arylrhodium species was ascertained. A catalytic cycle, commencing with the transmetalation, was thus proposed for the reaction.

## Introduction

Pd- or Ni-catalyzed cross-coupling of carbon electrophiles $R^+$ from aryl, alkenyl, or alkynyl halides with organometallic compounds of B, Si, Sn, Zn, and so on, is one of the most useful methods for constructing carbon−carbon bonds in organic synthesis.[1] In contrast to the thoroughly investigated Pd or Ni catalysis, the catalytic activity of other transition metals,[2] including Rh,[3] has been explored to a far less extent. The peculiar nature of Rh-complex catalysis, from the context that not only the common catalytic cycle commencing with oxidative addition but also one commencing with transmetalation are allowed, does deem it noteworthy (path A vs path B of Figure 1).[3b,4] Furthermore, the excellent catalytic activity of Rh has been realized recently in other types of cross-coupling of $R^+$ from carbonyl compounds or conjugated enones with arylmetallic compounds of B, Si, Bi, Ti, or Zn, where transmetalation has been known to be an essential step in the catalytic cycle.[5] From consideration of this phenomenon, it was envisaged that certain reactions, hitherto unsatisfactory results with Pd or Ni catalysis, may be affected by making use of a Rh catalyst when $R^+$ and/or organometallic compounds are appropriate for the reaction via path A. Among such reactions, the cross-coupling of arylzinc compounds with silylmethyl halides attracted our attention (Figure 2), as arylzinc compounds are prepared readily from aryl iodides and zinc powder with 100% atom efficiency,[6] and of which some are known to form Rh−Ar complexes.[7] Silylmethyl halides exhibit enhanced reactivity to Rh in oxidative addition, probably through a nucleophilic displacement

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(1) For review, see: (a) *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998. (b) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; John Wiley & Sons: New York, 2002. (c) Tsuji, J. *Palladium Reagents and Catalysis: Innovation in Organic* Synthesis; John Wiley & Sons: New York, 1995.

(2) For review, see: (a) Shinokubo, H.; Oshima, K. *Eur. J. Org. Chem.* **2004**, 2081−2091. (b) Beletskaya, I. P.; Cheprakov, A. V. *Coord. Chem. Rev.* **2004**, *248*, 2337−2364. (c) Fuerstner, A.; Martin, R. *Chem. Lett.* **2005**, *34*, 624−629.

(3) (a) Larock, R. C.; Hershberger, S. S. *J. Organomet. Chem.* **1982**, *225*, 31−41. (b) Larock, R. C.; Narayanan, K.; Hershberger, S. S. *J. Org. Chem.* **1983**, *48*, 4377−4380. (c) Andrianome, M.; Delmond, B. *J. Org. Chem.* **1988**, *53*, 542−545. (d) Andrianome, M.; Haberle, K.; Delmond, B. *Tetrahedron* **1989**, *45*, 1079−1088. (e) Hossain, K. M.; Takagi, K. *Chem. Lett.* **1999**, 1241−1242. (f) Ueura, K.; Satoh, T.; Miura, M. *Org. Lett.* **2005**, *7*, 2229−2231. (g) Evans, P. A.; Uraguchi, D. *J. Am. Chem. Soc.* **2003**, *125*, 7158−7159. (h) Evans, P. A.; Leahy, D. K. *J. Am. Chem. Soc.* **2003**, *125*, 8974−8975.

(4) (a) Schwartz, J.; Hart, D. W.; Holden, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 9269−9271. (b) Semmelhack, M. F.; Ryono, L. *Tetrahedron Lett.* **1973**, *14*, 2967−2970. (c) Hegedus, L. S.; Kendall, P. M.; Lo, S. M.; Sheats, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 5448−5452. (d) Fanizzi, F. P.; Sunley, G. J.; Maitlis, P. M. *J. Organomet. Chem.* **1987**, *330*, C31−C32.

(5) For review, see: (a) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169−196. (b) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829−2844.

(6) For our synthesis of arylzinc compounds, see: (a) Takagi, K. *Chem. Lett.* **1993**, 469−472. (b) Ogawa, Y.; Saiga, A.; Mori, M.; Shibata, T.; Takagi, K. *J. Org. Chem.* **2000**, *65*, 1031−1036. (c) Ikegami, R.; Koresawa, A.; Shibata, T.; Takagi, K. *J. Org. Chem.* **2003**, *68*, 2195−2199. Except for Zn, simple substances of other metals such as B, Si, Sn, Bi, or Ti are not applicable to the synthesis of arylmetal compounds from aryl halides as metallic sources.

(7) Krug, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 1674−1679.

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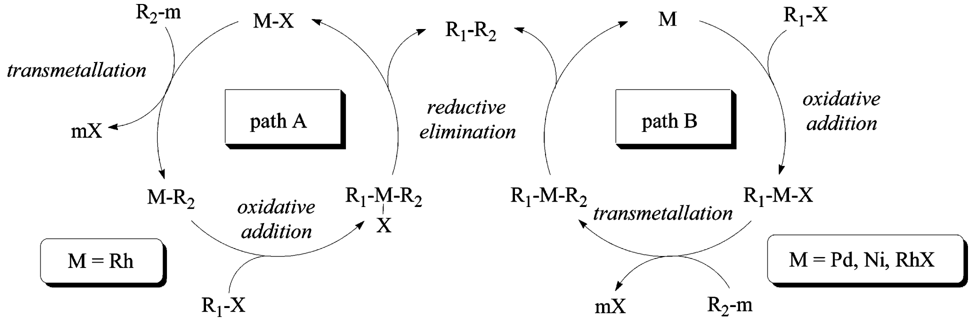


**FIGURE 1.** Two catalytic cycles for transition-metal-catalyzed cross-coupling.

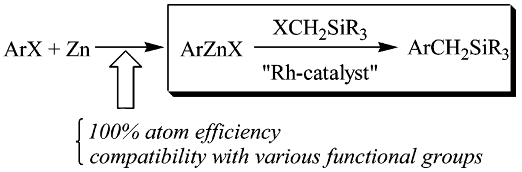
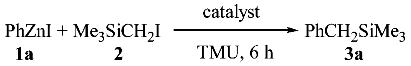


**FIGURE 2.** New entry in a synthetic method of functionalized benzylsilanes.

mechanism,[8,9] owing to the presence of a Si substituent at the α position, and lack undesirable side reactions such as the β elimination of the resulting oxidative adducts.

## Results and Discussion

**TABLE 1. Catalytic Synthesis of Benzylsilane 3a**[a]



$$\underset{\mathbf{1a}}{\mathrm{PhZnI}} + \underset{\mathbf{2}}{\mathrm{Me_3SiCH_2I}} \xrightarrow[\text{TMU, 6 h}]{\text{catalyst}} \underset{\mathbf{3a}}{\mathrm{PhCH_2SiMe_3}}$$

| entry | catalyst | temp (°C) | yield[b] (%) |
|---|---|---|---|
| 1 | 1:2 $[\mathrm{RhCl(cod)}]_2$/dppf | 40 | 93 |
| 2 | 1:2 $[\mathrm{RhCl(cod)}]_2$/dppf | rt | 86 |
| 3 | 1:2 $[\mathrm{RhCl(cod)}]_2$/$\mathrm{PPh_3}$ | 40 | <5 |
| 4 | 1:2 $[\mathrm{RhCl(cod)}]_2$/ttmpp[c] | 40 | 13 |
| 5 | 1:2 $[\mathrm{RhCl(cod)}]_2$/P(*t*-Bu)$_3$ | 40 | 67 |
| 6 | 1:2 $[\mathrm{RhCl(cod)}]_2$/dtbpb[d] | 40 | 59 |
| 7 | 1:2 $[\mathrm{RhCl(cod)}]_2$/dppp | 40 | 20 |
| 8 | 1:2 $[\mathrm{RhCl(cod)}]_2$/BINAP | 40 | 37 |
| 9 | $\mathrm{RhCl(PPh_3)_3}$ | rt | <5 |
| 10[e] | 1:2 $[\mathrm{RhCl(cod)}]_2$/dppf | 40 | 74 |
| 11[f] | 1:2 $[\mathrm{RhCl(cod)}]_2$/dppf | 40 | 10 |
| 12 | $\mathrm{Pd(PPh_3)_4}$ | rt | 6 |
| 13 | $\mathrm{Pd(dba)_2}$/P(*t*-Bu)$_3$ | rt | <5 |
| 14 | $\mathrm{PdCl_2(PhCN)_2}$/dppf[g] | rt | <5 |
| 15 | $\mathrm{NiBr_2}$/dppf[g] | rt | <5 |

[a] **1a** (1.2 mmol), **2** (1.0 mmol), catalyst (0.05 mmol), and TMU (0.6 mL) were employed for all entries except entry 2, where 0.1 mmol of catalyst was used. [b] GLC yield. [c] ttmpp = tris(2,4,6-trimethoxyphenyl)phosphine. [d] dtbpb = 2-(di-*tert*-butylphosphino)biphenyl. [e] DMF was used as solvent. [f] 2-Methoxyethyl ether was used as solvent. [g] With Zn (0.2 mmol).

A reaction solution composed of phenylzinc iodide (**1a**; 1.2 equiv), (iodomethyl)trimethylsilane (**2**; 1.0 equiv), and a Rh catalyst (5−10 mol %) in *N,N,N′,N′*-tetramethylurea (TMU) was stirred at 40 °C for 6 h under nitrogen (Table 1). Throughout this study, Rh catalysts were prepared in situ from $[\mathrm{RhCl(cod)}]_2$ (cod = 1,5-cyclooctadiene) and various phosphorus ligands (Rh/P = 1:2), among which Rh−dppf [dppf = 1,1′-bis(diphenylphosphino)ferrocene] exhibited excellent catalytic activity in the reaction, giving the desired coupling product **3a** in high yield (entry 1). Under the catalysis by Rh−dppf, the reaction also took place smoothly at ambient temperature, requiring 10 mol % of the catalyst (entry 2). Phosphorus ligands such as P(*t*-Bu)$_3$ and 2-(di-*tert*-butylphosphino)biphenyl gave the reactive Rh catalyst, but the selectivity was inferior to that of Rh−dppf, as biphenyl was produced in 31 and 40% yields, respectively, along with the desired product (entries 5 and 6). Other Rh catalysts, including the Wilkinson complex, were less effective, and the desired reaction took place slowly, if at all (entries 3, 4, and 7−9). Moreover, neither Pd nor Ni complexes, even ones containing dppf or P(*t*-Bu)$_3$, showed catalytic activity for this reaction (entries 12−15). As the reaction solvent, DMF was also suitable (entry 10), but 2-methoxyethyl ether was less effective than TMU (entry 11). (Chloromethyl)trimethylsilane could not replace **2** under the examined conditions. Various arylzinc compounds containing such functional groups as CN, $\mathrm{CO_2R}$, COPh, $\mathrm{CON(CH_3)_2}$, Cl, $\mathrm{OCH_3}$, $\mathrm{N(C_2H_5)_2}$, or $\mathrm{CH_2OAc}$ at the ortho, meta, or para position, **1b**−**m**, underwent catalysis by Rh−dppf in the reactions with **2** to afford the corresponding coupling products **3b**−**m** efficiently and in good to excellent yields, as shown in Table 2. Heteroaromatic compound **1n** was also tolerated in the reaction (entry 13).

In principle, there exist four kinds of cross-coupling reactions leading to benzylsilanes, with respect to the position of bond formation, $\mathrm{CH_2}$−Si or Ar−$\mathrm{CH_2}$, and the formal electronic charge of coupling partners, for example, $\mathrm{CH_2}^+ + \mathrm{Si}^-$ or $\mathrm{CH_2}^- + \mathrm{Si}^+$ (Figure 3).[10−13] Among these, the present combination is the least-studied one;[13] therefore, the reaction reported herein featuring a novel catalysis by Rh, the utility of readily available starting materials **1** and **2**, and a high degree of functional group tolerance provides a novel and useful synthetic method for the production of benzylsilanes, which are diversely employed as valuable synthetic intermediates in organic synthesis.[14]

Next, the catalytic efficiency of Rh−dppf toward other alkyl halides such as tributyl(iodomethyl)stannane (**4**)[15] or 3-iodo-2,2-dimethylpropane (**5**) was examined. Though both bear a structural resemblance to **2** with respect to the lack of a

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[8] Concerning the accelerating effect of α-silyl substituents on the reactivity of alkyl electrophiles for nucleophilic substitution reactions, see for example: (a) Oh, H. K.; Shin, C. H.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2411−2414. (b) Apeloig, Y.; Biton, R.; Abu-Freih, A. *J. Am. Chem. Soc.* **1993**, *115*, 2522−2523.

[9] Concerning the $\mathrm{S_N2}$ mechanism for oxidative addition of alkyl electrophiles to Rh(I), see for example: (a) Chauby, V.; Daran, J.-C.; Serra-Le Berre, C.; Malbosc, F.; Kalck, P.; Gonzalez, O. D.; Haslam, C. E.; Haynes, A. *Inorg. Chem.* **2002**, *41*, 3280−3290. (b) Ellis, P. R.; Pearson, J. M.; Haynes, A.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *Organometallics* **1994**, *13*, 3215−3226.

[10] K: (a) Corriu, R. J. P.; Guerin, C. *J. Chem. Soc., Chem. Commun.* **1980**, 168−169. Li: (b) Sekiguchi, A.; Nanjo, M.; Kabuto, C.; Sakurai, H. *Organometallics* **1995**, *14*, 2630−2632. Si/Pd: (c) Eaborn, C.; Griffiths, R. W.; Pidcock, A. *J. Organomet. Chem.* **1982**, *225*, 331−341.

$\beta$-hydrogen, their reactivity toward **1** was not necessarily similar to that of **2**, where the former afforded the desired products in moderate to good yields,[16] but the latter did not participate in any reactions (Scheme 1). Furthermore, iodoethane gave the protodezincation product of **1b** selectively under similar conditions. These results suggest that the presence of metallic substituents at the α carbon of the alkyl halides is beneficial for the Rh−dppf catalyzed cross-coupling of the halides with **1**.[8,9,17]

During the course of this study, we observed that the reddish brown color of Rh−dppf in TMU rapidly changed to dark green when **1**, for example **1b**, was added to the solution, which possibly indicates transmetalation between Rh−dppf and **1**. To gain accurate knowledge on the reaction, a preliminary $^{31}P$ NMR study was attempted using various solutions containing several of the reaction components prepared at room temperature (Figure 4).[18] Initially, the $^{31}P$ NMR of Rh−dppf, $[RhCl(cod)]_2$ and dppf, in TMU/$CH_3CN$-$d_3$ was measured to reveal that the Rh−dppf is composed of several species in the solution, including $[RhCl(dppf)]_2$ as a major component.[19] The subsequent addition of 1.0 equiv of **1b** to the solution of Rh−dppf to give Rh−dppf−**1b** afforded the completely different $^{31}P$ NMR spectrum from that of Rh−dppf, which was too complex to assign. Fortunately, the $^{31}P$ NMR spectrum of Rh−dppf−**1b** in the copresence of 1.0 equiv of $PPh_3$ to give Rh−dppf−$PPh_3$−**1b** in TMU/$CH_3CN$-$d_3$[21] or Rh−dppf−**1b** in DMSO-$d_6$[22] showed the doublet of triplets or the doublet of doublet signals with $J_{Rh-P} = 121$ or 124 Hz, respectively, in accord with the formation of a Rh−Ar bond.[23] Simultaneously, the signals of Rh−dppf disappeared completely. Alternatively, the addition of 20 equiv of **2** to the TMU/$CH_3CN$-$d_3$ solution of Rh−dppf at 40 °C, in contrast, did not change the $^{31}P$ NMR spectrum from that of Rh−dppf. These results suggest that the reaction of **1** with Rh−dppf takes place quantitatively at room temperature with only a stoichiometric amount of **1**, while the reaction of **2** with Rh−dppf, even at 40 °C with an excess amount of **2**, does not.

Therefore, under catalytic conditions (Rh−dppf/**1**/**2** = 0.05−0.1:1:1 from room temperature to 40 °C), the former reaction must overwhelmingly precede the latter reaction. Thus, the Rh−Ar species generated possess higher reactivity toward **2** in an $S_N$-type oxidative addition compared with that of Rh−dppf,[4c] which probably enables the alkyl substrates, **2**, which are inactive coupling partners in path B, to be incorporated into the catalytic reaction taking path A (Figure 1).

In conclusion, the synthesis of benzylsilanes from the hitherto least employed combination of coupling partners, ArM + $XCH_2$-

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(11) Li: (a) Hultzsch, K. C.; Bonitatebus, P. J.; Jernelius, J.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2001**, *20*, 4705−4712. (b) Kyushin, S.; Ikarugi, M.; Tsunakawa, S.; Izumi, Y.; Miyake, M.; Sato, M.; Matsumoto, H.; Goto, M. *J. Organomet. Chem.* **1994**, *473*, 19−27. (c) Kanda, T.; Kato, S.; Sugino, T.; Kambe, N.; Sonoda, N. *J. Organomet. Chem.* **1994**, *473*, 71−83. (d) Engelhardt, L. M.; Leung, W. P.; Raston, C. L.; Salem, G.; Twiss, P.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1988**, 2403−2409. (e) Carpenter, T. A.; Evans, G. E.; Leeper, F. J.; Staunton, J.; Wilkinson, M. R. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1043−1051. (f) Musker, W. K.; Scholl, R. L. *J. Organomet. Chem.* **1971**, *27*, 37−43. Mg: (g) Allen, J. M.; Aprahamian, S. L.; Sans, E. A.; Shechter, H. *J. Org. Chem.* **2002**, *67*, 3561−3574. (h) De Boer, H. J. R.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1987**, *321*, 291−306. (i) Coughlin, D. J.; Salomon, R. G. *J. Org. Chem.* **1979**, *44*, 3784−3790.

(12) Al/Pd: (a) Saulnier, M. G.; Kadow, J. F.; Tun, M. M.; Langley, D. R.; Vyas, D. M. *J. Am. Chem. Soc.* **1989**, *111*, 8320−8321. B/Pd: (b) Molander, G. A.; Yun, C.-S.; Ribagorda, M.; Biolatto, B. *J. Org. Chem.* **2003**, *68*, 5534−5539. (c) Zou, G.; Reddy, Y. K.; Falck, J. R. *Tetrahedron Lett.* **2001**, *42*, 7213−7215. (d) Soderquist, J. A.; Santiago, B.; Rivera, I. *Tetrahedron Lett.* **1990**, 31, 4981−4984. Cu: (e) Lappert, M. F.; Pearce, R. *J. Chem. Soc., Chem. Commun.* **1973**, 24−25. In/Pd: (f) Perez, I.; Sestelo, J. P.; Sarandeses, L. A. *J. Am. Chem. Soc.* **2001**, *123*, 4155−4160. Mg/Ni: (g) Organ, M. G.; Murray, A. P. *J. Org. Chem.* **1997**, *62*, 1523−1526. (h) Brondani, D. J.; Corriu, R. J. P.; El Ayoubi, S.; Moreau, J. J. E.; Man, M. W. C. *Tetrahedron Lett.* **1993**, *34*, 2111−2114. (i) Sengupta, S.; Leite, M.; Raslan, D. S.; Quesnelle, C.; Snieckus, V. *J. Org. Chem.* **1992**, *57*, 4066−4068. (j) Kitching, W.; Olszowy, H. A.; Schott, I.; Adcock, W.; Cox, D. P. *J. Organomet. Chem.* **1986**, *310*, 269−284. (k) Tamao, K.; Ishida, N.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2120−2122. (l) Hayashi, T.; Katsuro, Y.; Okamoto, Y.; Kumada, M. *Tetrahedron Lett.* **1981**, *22*, 4449−4452. (m) Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958−1969. Mg/Pd: (n) Negishi, E.; Luo, F.-T.; Rand, C. L. *Tetrahedron Lett.* **1982**, *23*, 27−30. Sn/Pd: (o) Itami, K.; Mineno, M.; Kamei, T.; Yoshida, J. *Org. Lett.* **2002**, *4*, 3635−3638. (p) Itami, K.; Kamei, T.; Yoshida, J. *J. Am. Chem. Soc.* **2001**, *123*, 8773−8779. Zn/Pd: (q) Abarbri, M.; Parrain, J.-L.; Kitamura, M.; Noyori, R.; Duchene, A. *J. Org. Chem.* **2000**, *65*, 7475−7478. Reference 12k.

(13) Cu: Majetich, G.; Leigh, A. J. *Tetrahedron Lett.* **1991**, *32*, 609−610. Mg/Cu: Reference 11g.

(14) Concerning the utility of **3** as the synthetic equivalent of benzyl anions, see for example: (a) Chan, T. H.; Pellon, P. *J. Am. Chem. Soc.* **1989**, *111*, 8737−8738. (b) Askari, S.; Lee, S.; Perkins, R. R.; Scheffer, J. R. *Can. J. Chem.* **1985**, *63*, 3526−3529. (c) Aono, M.; Terao, Y.; Achiwa, K. *Chem. Lett.* **1985**, 339−340. (d) Kanemasa, S.; Tanaka, J.; Nagahama, H.; Tsuge, O. *Chem. Lett.* **1985**, 1223−1226. (e) Bennetau, B.; Dunogues, J. *Tetrahedron Lett.* **1983**, *24*, 4217−4218. (f) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1982**, *104*, 7609−7622. Reference 12p. Concerning the utility of **3** as the precursor of benzyl alcohols, benzaldehydes, bibenzyls, or 4-alkylidenecyclohexenes, see for example: (g) Cermenati, L.; Fagnoni, M.; Albini, A. *Can. J. Chem.* **2003**, *81*, 560−566. (h) Hirao, T.; Morimoto, C.; Takada, T.; Sakurai, H. *Tetrahedron* **2001**, *57*, 5073−5079. (i) Fujii, T.; Hirao, T.; Ohshiro, Y. *Tetrahedron Lett.* **1993**, *34*, 5601−5604. (j) Yoshida, J.; Murata, T.; Isoe, S. *Tetrahedron Lett.* **1986**, *27*, 3373−3376. References 11i and 12k.

(15) Seyferth, D.; Andrews, S. B. *J. Organomet. Chem.* **1971**, *30*, 151−166.

(16) Three kinds of cross-couplings have been applied to the synthesis of benzylstannanes, $ArCH_2Sn$. For the combination of $ArCH_2M$ (M = Li, Mg, or Zn) + XSn, see for example: (a) Labadie, J. W.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6129−6137. (b) Berk, S. C.; Yeh, M. C. P.; Jeong, N.; Knochel, P. *Organometallics* **1990**, *9*, 3053−3064. (c) Marton, D.; Russo, U.; Stivanello, D.; Tagliavini, G.; Ganis, P.; Valle, G. C. *Organometallics* **1996**, *15*, 1645−1650. (d) Zhu, X.; Blough, B. E.; Carroll, F. I. *Tetrahedron Lett.* **2000**, *41*, 9219−9222. For the combination of SnM (M = K, Li, or Sn/Pd) + $XCH_2Ar$, see: (e) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *197*, C19−C21. (f) Tius, M. A.; Gomez-Galeno, J. *Tetrahedron Lett.* **1986**, *27*, 2571−2574. (g) Azarian, D.; Dua, S. S.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1976**, *117*, C55−C57. Reference 16a. For the combination of $SnCH_2M$ (M = Mg/Ni or Zn/Pd) + XAr, see: (h) Sato, T.; Kawase, A.; Hirose, T. *Synlett* **1992**, 891−892. Reference 12j. However, to our knowledge, the combination of ArM + $XCH_2Sn$ has not been applied to the synthesis yet.

(17) Nevertheless, both halides **2** and **4** are less reactive than iodomethane as a coupling partner with **1** under the catalysis by Rh−dppf.[3e]

(18) $^{31}P$ NMR spectra are summarized in Supporting Information.

(19) Major signals that appeared at $\delta$ 52.2 (d, $J_{Rh-P} = 202$ Hz) could be assigned to $[RhCl(dppf)]_2$. The numerical value is close to that of $[RhCl(P(i\text{-}Pr)_3)_2]_2$ $\delta$ 60.64 (d, $J_{Rh-P} = 197.2$ Hz)[20] or of $[RhCl((S)\text{-binap})]_2$ $\delta$ 49.7 (d, $J_{Rh-P} = 197$ Hz).[23] The second signals that appeared at $\delta$ 52.4 (dd, $J_{Rh-P} = 182$ Hz) and $\delta$ 47.2 (dd, $J_{Rh-P} = 182$ Hz, $J_{P-P} = 43$ Hz) could be tentatively assigned to RhCl(L)(dppf), L = cod or solvent, where the former is partly overlapped with the major ones.

(20) Binger, P.; Haas, J.; Glasser, G.; Goddard, R.; Krueger, C. *Chem. Ber.* **1994**, *127*, 1927−1929.

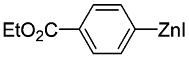
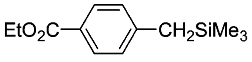
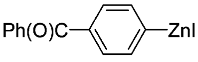
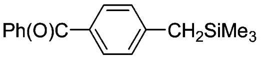
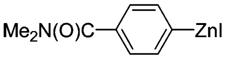
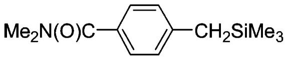
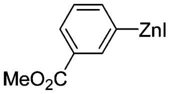
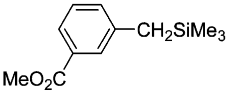
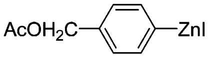
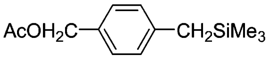
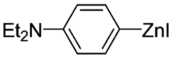
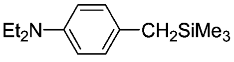
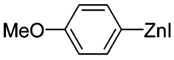
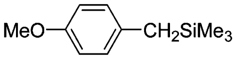
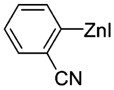
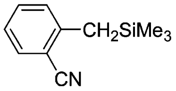
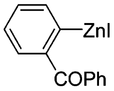
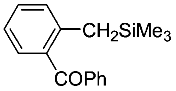
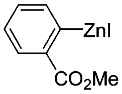
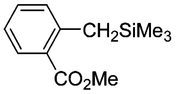
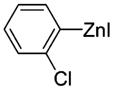
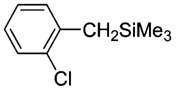
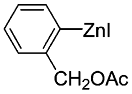
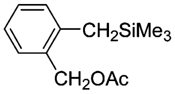
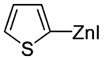
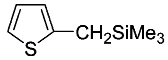
(21) The major signals that appeared at $\delta$ 43.3 (ddd, $J_{P-P} = 308$ Hz, $J_{Rh-P} = 177$ Hz, $J_{P-P} = 31.7$ Hz), 34.4 (dt, $J_{Rh-P} = 121$ Hz, $J_{P-P} = 33.1$ Hz), and 27.5 (ddd, $J_{P-P} = 308$ Hz, $J_{Rh-P} = 173$ Hz, $J_{P-P} = 34.8$ Hz) could be assigned to $RhAr(PPh_3)(dppf)$. The numerical value is similar to that of $RhPh(PPh_3)[(S)\text{-binap}]$ $\delta$ 35.4 (ddd, $J_{Rh-P} = 121$ Hz, $J_{P-P} = 39$ Hz, $J_{P-P} = 30$ Hz), 32.8 (ddd, $J_{P-P} = 375$ Hz, $J_{Rh-P} = 144$ Hz, $J_{P-P} = 43$ Hz), and 29.6 (ddd, $J_{P-P} = 375$ Hz, $J_{Rh-P} = 143$ Hz, $J_{P-P} = 36$ Hz).[23]

(22) The major signals that appeared at $\delta$ 42.3 (dd, $J_{Rh-P} = 183$ Hz, $J_{P-P} = 29$ Hz) and $\delta$ 30.2 (dd, $J_{Rh-P} = 124$ Hz, $J_{P-P} = 29$ Hz) could be tentatively assigned to RhAr(L)(dppf), L = cod or solvent. For DMSO as a ligand for Rh, see for example: Dorta, R.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Chem.−Eur. J.* **2003**, *9*, 5237−5249.

(23) Hayashi, T.; Takahashi, M.; Takaya, Y.; Ogasawara, M. *J. Am. Chem. Soc.* **2002**, *124*, 5052−5058.

**TABLE 2. Synthesis of Functionalized Benzylsilanes**[a]

$$\underset{\textbf{1b-1n}}{\mathrm{ArZnX}} + \underset{\textbf{2}}{\mathrm{Me_3SiCH_2I}} \xrightarrow[\text{TMU, 40 °C}]{\text{Rh-dppf}} \underset{\textbf{3b-3n}}{\mathrm{ArCH_2SiMe_3}}$$

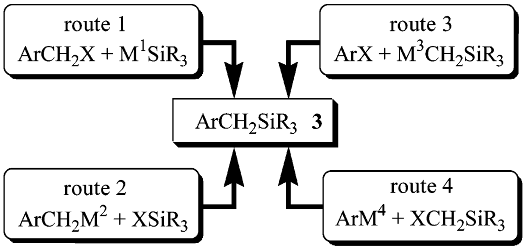
| entry | ArZnX | | $ArCH_2SiMe_3$ | | yield[b] (%) |
|---|---|---|---|---|---|
| 1 |  | **1b** |  | **3b** | 87 |
| 2 |  | **1c** |  | **3c** | 95 |
| 3 |  | **1d** |  | **3d** | 68 |
| 4 |  | **1e** |  | **3e** | 95 |
| 5 |  | **1f** |  | **3f** | 66 |
| 6 |  | **1g** |  | **3g** | 68 |
| 7 |  | **1h** |  | **3h** | 85 |
| 8 |  | **1i** |  | **3i** | 90 |
| 9 |  | **1j** |  | **3j** | 73 |
| 10 |  | **1k** |  | **3k** | 58 |
| 11 |  | **1l** |  | **3l** | 82 |
| 12 |  | **1m** |  | **3m** | 73 |
| 13 |  | **1n** |  | **3n** | 73 |

[a] **1b**−**n** (0.44 mmol), **2** (0.4 mmol), and TMU (0.25 mL) were employed in all entries. In entries 1, 3, 4, 6, and 7, 0.01 mmol of $[RhCl(cod)]_2$ and 0.02 mmol of dppf were used, whereas 0.02 mmol of $[RhCl(cod)]_2$ and 0.04 mmol of dppf were used in entries 2, 5, and 8−13. The reaction time was 12 h for entries 1, 4, 9, and 12, 6 h for entries 3, 5−7, 10, 11, and 13, 24 h for entry 2, and 72 h for entry 8. [b] Isolated yield.

Si, has been accomplished, taking advantage of the novel catalytic nature of the Rh complex. Characteristics of the reaction such as the utility of readily available starting materials, the great degree of functional group tolerance, and the simplicity of the employed procedure make the reaction useful for synthesizing benzylsilanes as valuable intermediates in organic synthesis.

## Experimental Section

All reactions were performed under an atmosphere of nitrogen in oven-dried glassware. TMU was distilled under nitrogen and stored over 4-Å molecular sieves. Phenyl(4-iodophenyl)methanone,[24] phenyl(2-iodophenyl)methanone,[24] (4-iodophenyl)methyl acetate,[25] (2-iodophenyl)methyl acetate,[25] *N*,*N*-diethyl-4-iodoben-



$M^1$ = K, Li, or Si + Pd cat.: ref 10; $M^2$ = Li or Mg: ref 11;
$M^3$ = Cu or Al, B, In, Mg, Sn, or Zn + Pd or Ni cat.: ref 12;
$M^4$ = Cu or Mg + Cu cat.: ref 13.

**FIGURE 3.** Cross-coupling routes to **3**.

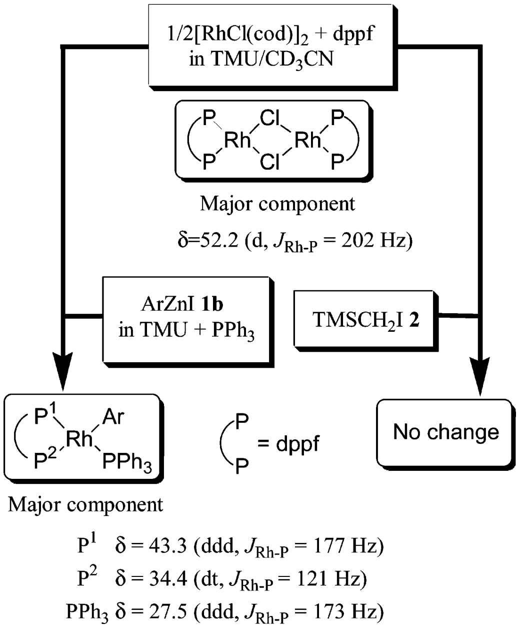
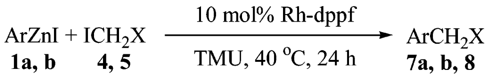


**FIGURE 4.** $^{31}P$ NMR of Rh−phosphine complexes.

**SCHEME 1**



$$\underset{\textbf{1a, b}}{ArZnI} + \underset{\textbf{4, 5}}{ICH_2X} \xrightarrow[\text{TMU, 40 °C, 24 h}]{\text{10 mol\% Rh-dppf}} \underset{\textbf{7a, b, 8}}{ArCH_2X}$$

**7a**; X=$SnBu_3$, Ar=$C_6H_5$ 73%
**7b**; X=$SnBu_3$, Ar=*p*-$EtO_2CC_6H_4$ 60%
**8**; X=$CMe_3$, Ar=$C_6H_5$ 0%

zenamine,[26] 2-iodobenzonitrile,[24] and **4**[15] were prepared following the literature methods. Other compounds including Zn powder were purchased from a commercial supplier and used without further purification. The NMR spectra were recorded in $CDCl_3$ at 300 MHz for $^1H$ or 75.5 MHz for $^{13}C$ with TMS or chloroform-$d_1$ as the internal standard, respectively.

**Preparation of Ethyl 4-[(Trimethylsilyl)methyl]benzoate (3b): Representative Procedure.** To $[RhCl(cod)]_2$ (6.2 mg, 0.013 mmol) and dppf (13.9 mg, 0.025 mmol) was added a TMU solution of arylzinc iodide **1b** (0.32 mL, 0.55 mmol) with stirring for 30 min at room temperature. (Iodomethyl)trimethylsilane (**2**; 0.074 mL, 0.5 mmol) was added to the solution and stirred for 12 h at 40 °C. The resulting mixture was quenched by the addition of aqueous HCl. The work up, extracting with ether, washing with aqueous HCl, drying over $MgSO_4$, and evaporating the solvent, afforded a crude product, which was chromatographed on silica gel with a hexane/ethyl acetate (10:1) eluent to afford 102.8 mg of **3b** (87%): oil; IR (neat) 1717, 1278, 1108, 855 $cm^{-1}$; $^1H$ NMR $\delta$ −0.01 (s, 9H), 1.38 (t, $J$ = 7.0 Hz, 3H), 2.16 (s, 2H), 4.35 (q, $J$ = 7.0 Hz, 2H), 7.04 (d, $J$ = 8.3 Hz, 2H), 7.90 (d, $J$ = 8.3 Hz, 2H); $^{13}C$ NMR $\delta$ −2.0, 14.3, 27.9, 60.6, 126.2, 127.8, 129.5, 146.6, 166.8; HRMS calcd for $C_{13}H_{20}O_2Si$, 236.1233; found, 236.1236 ($M^+$).

***N,N*-Dimethyl-4-[(trimethylsilyl)methyl]benzamide (3d)**: oil; IR (neat) 1638, 1392, 1249, 853 $cm^{-1}$; $^1H$ NMR $\delta$ −0.04 (s, 9H), 2.08 (s, 2H), 2.98 (s, 3H), 3.04 (s, 3H), 6.98 (d, $J$ = 8.0 Hz), 7.26 (d, $J$ = 8.0 Hz); $^{13}C$ NMR $\delta$ −2.1, 27.2, 35.3, 39.6, 127.1, 127.6, 131.6, 142.5, 172.0; HRMS calcd for $C_{13}H_{21}NOSi$, 235.1392; found, 235.1400 ($M^+$).

**Methyl 3-[(Trimethylsilyl)methyl]benzoate (3e)**: oil; IR (neat) 1725, 1284, 851 $cm^{-1}$; $^1H$ NMR $\delta$ −0.01 (s, 9H), 2.13 (s, 2H), 3.89 (s, 2H), 7.19 (d, $J$ = 7.5 Hz, 1H), 7.28 (t, $J$ = 7.5 Hz, 1H), 7.68 (s, 1H), 7.75 (d, $J$ = 7.5 Hz, 1H); $^{13}C$ NMR $\delta$ −2.0, 26.9, 52.0, 125.2, 128.1, 128.9, 129.9, 132.5, 140.9, 167.4; HRMS calcd for $C_{12}H_{18}SiO_2$, 222.1076; found, 222.1079 ($M^+$).

**4-[(Trimethylsilyl)methyl]phenyl Acetate (3f)**: oil; IR (neat) 1744, 1249, 1021, 851 $cm^{-1}$; $^1H$ NMR $\delta$ 0.00 (s, 9H), 2.09 (s, 2H), 2.09 (s, 3H), 5.06 (s, 2H), 7.00 (d, $J$ = 7.8 Hz), 7.22 (d, $J$ = 7.8 Hz); $^{13}C$ NMR $\delta$ −2.0, 21.0, 26.8, 66.3, 128.1, 128.3, 131.2, 140.7, 170.9; HRMS calcd for $C_{13}H_{20}O_2Si$, 236.1233; found, 236.1234 ($M^+$).

***N,N*-Diethyl-4-[(trimethylsilyl)methyl]benzenamine (3g)**: oil; IR (neat) 1615, 1518, 1263, 845 $cm^{-1}$; $^1H$ NMR $\delta$ 0.02 (s, 9H), 1.16 (t, $J$ = 7.2 Hz, 3H), 1.98 (s, 2H), 3.32 (q, $J$ = 7.2 Hz, 2H), 6.64 (d, $J$ = 8.7 Hz, 2H), 6.88 (d, $J$ = 8.7 Hz, 2H); $^{13}C$ NMR $\delta$ −1.9, 12.6, 25.2, 44.5, 112.9, 127.5, 128.8, 144.9; HRMS calcd for $C_{14}H_{25}NSi$, 235.1756; found, 235.1759 ($M^+$).

**Phenyl{2-[(trimethylsilyl)methyl]phenyl}methanone (3j)**: oil; IR (neat) 1663, 1265, 849, 702 $cm^{-1}$; $^1H$ NMR $\delta$ −0.05 (s, 9H), 2.35 (s, 2H), 7.12−7.16 (m, 2H), 7.30−7.36 (m, 2H), 7.42−7.47 (m, 2H), 7.54−7.56 (m, 1H), 7.78−7.82 (m, 2H); $^{13}C$ NMR $\delta$ −1.1, 24.5, 123.5, 123.5, 128.5, 130.2, 130.5, 131.5, 133.0, 136.6, 138.5, 141.3, 198.7; HRMS calcd for $C_{17}H_{20}OSi$, 268.1283; found, 268.1285 ($M^+$).

**Ethyl 4-[(Tributylstannyl)methyl]benzoate (7b)**: oil; IR (neat) 1717, 1276, 1106, 772 $cm^{-1}$; $^1H$ NMR $\delta$ 0.79−0.91 (m, 15H), 1.20−1.32 (m, 6H), 1.36−1.48 (m, 9H), 2.37 (t, $J$ = 28.2 Hz, 2H), 4.34 (q, $J$ = 7.2 Hz, 6H), 7.01 (d, $J$ = 8.3 Hz, 2H), 7.85 (d, $J$ = 8.3 Hz, 2H); $^{13}C$ $\delta$ 9.4, 13.7, 14.4, 19.3, 27.3, 28.9, 60.5, 124.9, 126.6, 129.7, 150.4, 166.9; HRMS calcd for $C_{22}H_{38}O_2Sn$, 454.1894; found, 454.1873 ($M^+$).

**2-Chloro[(trimethylsilyl)methyl]benzene (3l)**:[27] $^1H$ NMR $\delta$ 0.03 (s, 9H), 2.28 (s, 2H), 6.98−7.13 (m, 3H), 7.29 (d, $J$ = 7.8 Hz, 1H); $^{13}C$ NMR $\delta$ −1.5, 24.3, 125.2, 126.3, 129.3, 129.7, 132.6, 138.8.

**Benzyltrimethylsilane (3a).** See ref 28.[28]

**Phenyl{4-[(trimethylsilyl)methyl]}methanone (3c).** See ref 29.[29]

**4-Methoxy[(trimethylsilyl)methyl]benzene (3h).** See ref 11j.

**2-[(Trimethylsilyl)methyl]benzonitrile (3i).** See ref 12b.

**Methyl 2-[(trimethylsilyl)methyl]benzoate (3k).** See ref 14e.

**2-[(Trimethylsilyl)methyl]phenyl acetate (3m).** See ref 12d.

**2-[(Trimethylsilyl)methyl]thiophene (3n).** See ref 30.[30]

**Benzyltributylstannane (7a).** See ref 31.[31]

**Supporting Information Available:** General procedure for the synthesis of arylzinc compounds, Figures S3−S25 of $^1H$ NMR or $^{13}C$ NMR spectra of compounds **3a**−**n**, **7a**, and **7b**, and Figures S26−S33 of $^{31}P$ NMR spectra of Rh complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0520994

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(24) Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 14844−14845.

(25) Miles, J. A.; Grabiak, R. C.; Cummins, C. *J. Org. Chem.* **1982**, *47*, 1677−1682.

(26) Adimurthy, S.; Ramachandraiah, G.; Ghosh, P. K.; Bedekar, A. V. *Tetrahedron Lett.* **2003**, *44*, 5099−5101.

(27) Eaborn, C.; Parker, S. H. *J. Chem. Soc.* **1954**, 939−941.

(28) Guijarro, D.; Mancheno, B.; Yus, M. *Tetrahedron* **1994**, *50*, 8551−8558.

(29) Fuerstner, A.; Seidel, G. *Tetrahedron* **1995**, *51*, 11165−11176.

(30) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347−3354.

(31) Soundararajan, N.; Plutz, M. S. *Tetrahedron Lett.* **1987**, *28*, 2813−2816.