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Activator-free oxidative homocoupling of organosilanes catalysed by a palladium–DPPP complex†

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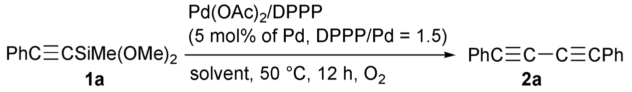
Oxidative homocoupling reaction of aryl- or alkynylsilanes was found to proceed without any added activators using a catalytic amount of a palladium–1,3-bis(diphenylphosphino)propane complex, affording the corresponding biaryls or 1,3-diynes in modest to excellent yields.

Palladium-catalysed carbon–carbon bond forming reactions using organosilanes, such as cross-coupling reaction (Hiyama coupling),[1] have recently received much attention as a promising alternative to those using organoboranes or organostannanes owing to their higher chemoselectivities and widespread availability. However, because of the weakly polarized character of a carbon–silicon bond of organosilanes, addition of an activator such as a fluoride ion,[1] a strong base,[2a–c] a copper(I) salt[2d] or a silver(I) salt[2e] is often indispensable for the reactions to proceed, and therefore, examples of the successful reactions free from the added activator are to the best of our knowledge totally limited to the cross-coupling with allyl carbonates[3a] or diene monoxides,[3b] and the Mizoroki–Heck type reaction with alkenes.[4] Herein we report the palladium–1,3-bis(diphenylphosphino)propane (DPPP) complex-catalysed oxidative homocoupling[5,6] as a novel entry for the activator-free carbon–carbon bond forming reaction using organosilanes.

First we investigated the reaction of dimethoxy(methyl)(phenylethynyl)silane (**1a**) in dimethyl sulfoxide (DMSO) at 50 °C for 12 h without any added activators using a palladium–DPPP complex under an oxygen atmosphere, and observed that the homocoupling product, 1,4-diphenylbutadiyne (**2a**), was produced in 70% yield (Table 1, Entry 1). The reaction proceeded as well in DMF to give a 35% yield of **2a** (Entry 2), whereas no trace of **2a** was detected in THF or toluene at all (Entries 3 and 4), indicating that a polar solvent plays an important role in this homocoupling. The use of a palladium–triphenylphosphine (PPh_3) complex or a ligandless palladium salt in lieu of the Pd–DPPP complex reduced the yield considerably (Entries 5 and 6). When the homocoupling reaction was carried out under a strictly prepared argon atmosphere, **2a** was scarcely generated (Entry 7). In contrast to **1a**, trimethyl(phenylethynyl)silane gave **2a** only in 18% yield, which implies that introduction of an electron-withdrawing group (methoxy group) on a silicon atom is necessary for the smooth reaction (Entry 8).

Under the optimized conditions, the homocoupling of various organosilanes **1** was next examined (Scheme 1). The results are summarized in Table 2. Similarly to the case of **1a**, the homocoupling of (1-naphthyl)- (**1b**) or (1-cyclohexenyl)ethynylsilane (**1c**) readily proceeded to provide the corresponding 1,3-butadiyne (**2b** or **2c**) in moderate yield (Entries 1–3). It should be noted that the homocoupling was also applicable to an arylsilane by employing an organosilanol instead of an organodialkoxysilane as a silicon reagent. In this case, addition of water improved the product yields significantly.[7] Thus, when dimethyl(phenyl)silanol (**1d**) was treated in DMSO–H_2O, the homocoupling product, biphenyl (**2d**), was produced in 70% yield (Entry 4). Similarly, arylsilanols bearing an electron-donating group at the *para*-position (**1e–1h**) also furnished high yields of biaryl **2e–2h** (Entries 5–8), whereas the reaction of an electron-deficient arylsilanol (**1i**) resulted in low yield (Entry 9). The reaction of other silanols bearing a *meta*-substituted phenyl (**1j–1l**), 3,4-(methylenedioxy)phenyl (**1m**) or 2-naphthyl group (**1n**) also took place smoothly, providing the respective homocoupling products (**2j–2n**) in high yields (Entries 10–14). On the other hand, *ortho*-substituted arylsilanols (**1o** and **1p**) or a heteroarylsilanol (**1q**) reacted sluggishly, leading to the formation of the products (**2o–2q**) in low to moderate yields (Entries 15–17). Worthy of note is that the present reaction conditions allow the employment of a fluoride ion-sensitive arylsilanol (**1r** or **1s**), whose C–$SiMe_3$ bond remained intact after the reaction (Entries 18 and 19).

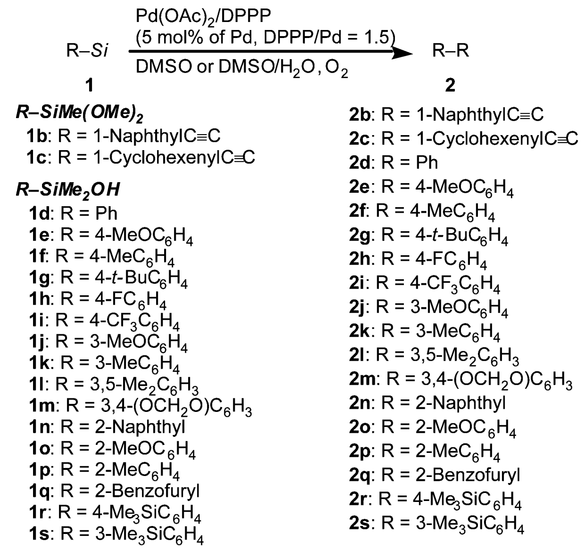
Table 1 Palladium-catalysed homocoupling of (phenylethynyl)silanes[a]



$$\underset{\textbf{1a}}{PhC\equiv CSiMe(OMe)_2} \xrightarrow[\text{solvent, 50 °C, 12 h, } O_2]{\text{Pd(OAc)}_2\text{/DPPP (5 mol\% of Pd, DPPP/Pd = 1.5)}} \underset{\textbf{2a}}{PhC\equiv C-C\equiv CPh}$$

Entry	Ligand	Solvent	Yield (%)[b]
1	DPPP	DMSO	70
2	DPPP	DMF	35
3	DPPP	THF	0
4	DPPP	toluene	0
5[c]	PPh_3	DMSO	11
6	—	DMSO	6
7[d]	DPPP	DMSO	11
8[e]	DPPP	DMSO	18

[a] The reaction was carried out in a solvent (1.3 mL) at 50 °C using **1a** (0.27 mmol) for 12 h in the presence of $Pd(OAc)_2$ (0.013 mmol) and DPPP (0.020 mmol) under an oxygen atmosphere. [b] GC yield. [c] $PPh_3/Pd = 3$. [d] Under an argon atmosphere. [e] Trimethyl(phenylethynyl)silane was used instead of **1a**.



R–SiMe(OMe)$_2$
1b: R = 1-NaphthylC≡C
1c: R = 1-CyclohexenylC≡C

R–SiMe$_2$OH
1d: R = Ph
1e: R = 4-$MeOC_6H_4$
1f: R = 4-MeC_6H_4
1g: R = 4-*t*-BuC_6H_4
1h: R = 4-FC_6H_4
1i: R = 4-$CF_3C_6H_4$
1j: R = 3-$MeOC_6H_4$
1k: R = 3-MeC_6H_4
1l: R = 3,5-$Me_2C_6H_3$
1m: R = 3,4-(OCH_2O)C_6H_3
1n: R = 2-Naphthyl
1o: R = 2-$MeOC_6H_4$
1p: R = 2-MeC_6H_4
1q: R = 2-Benzofuryl
1r: R = 4-$Me_3SiC_6H_4$
1s: R = 3-$Me_3SiC_6H_4$

2b: R = 1-NaphthylC≡C
2c: R = 1-CyclohexenylC≡C
2d: R = Ph
2e: R = 4-$MeOC_6H_4$
2f: R = 4-MeC_6H_4
2g: R = 4-*t*-BuC_6H_4
2h: R = 4-FC_6H_4
2i: R = 4-$CF_3C_6H_4$
2j: R = 3-$MeOC_6H_4$
2k: R = 3-MeC_6H_4
2l: R = 3,5-$Me_2C_6H_3$
2m: R = 3,4-(OCH_2O)C_6H_3
2n: R = 2-Naphthyl
2o: R = 2-$MeOC_6H_4$
2p: R = 2-MeC_6H_4
2q: R = 2-Benzofuryl
2r: R = 4-$Me_3SiC_6H_4$
2s: R = 3-$Me_3SiC_6H_4$

Scheme 1

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† Electronic supplementary information (ESI) available: experimental procedures and characterization data. See http://www.rsc.org/suppdata/cc/b3/b303852a/

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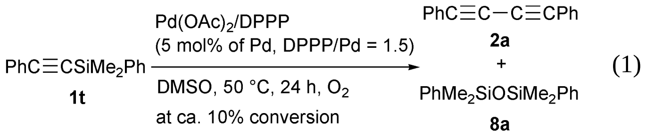


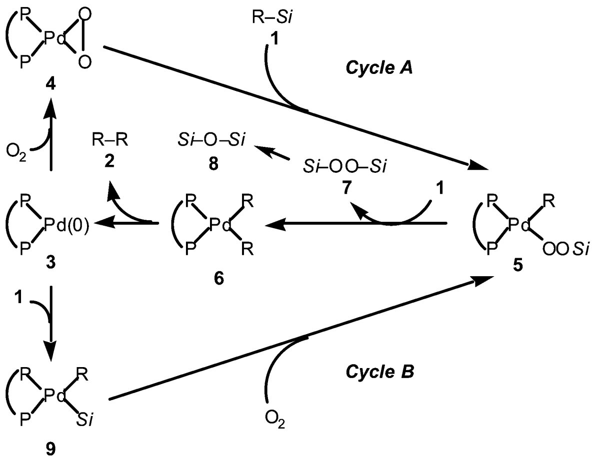
$$\underset{\mathbf{1t}}{\mathrm{PhC{\equiv}CSiMe_2Ph}} \xrightarrow[\text{DMSO, 50 °C, 24 h, } O_2 \text{ at ca. 10\% conversion}]{Pd(OAc)_2/DPPP \text{ (5 mol\% of Pd, DPPP/Pd = 1.5)}} \underset{\mathbf{2a}}{\mathrm{PhC{\equiv}C{-}C{\equiv}CPh}} + \underset{\mathbf{8a}}{\mathrm{PhMe_2SiOSiMe_2Ph}} \qquad (1)$$

Scheme 2 depicts two plausible catalytic cycles of the homocoupling reaction. Cycle A includes the formation of palladium(II) peroxide complex **4** resulting from the reaction of palladium(0) complex **3** with molecular oxygen as reported previously.[8] Subsequently, 2 mol of organic moieties in **1** would transmetalate to a palladium(II) complex to provide diorganopalladium complex **6** *via* complex **5**,[9] followed by reductive elimination of homocoupling product **2** with regenerating **3**. Alternatively, complex **5** is formed through insertion of oxygen into a Pd–Si bond of complex **9**, which is generated by oxidative addition of **1** to **3** (Cycle B).[10] At present, no definitive evidence is available that determines the reaction pathway. The ultimate fate of a silyl moiety has been identified to be disiloxane **8** through intermediary silyl peroxide **7**, as verified by the homocoupling of dimethyl(phenyl)(phenylethynyl)silane (**1t**), where 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane (**8a**) was detected by GC-MS spectrum of the reaction mixture along with 10% yield of **2a** (eqn. 1). The smooth homocoupling observed only in a polar solvent can be rationally explained by assuming that the solvent would coordinate to a Lewis acidic silicon atom of **1**, induced by an electron-withdrawing oxygen atom, to form a pentacoordinate species, which may be subject to the transmetalation (Cycle A)[11] or the oxidative addition (Cycle B).

Table 2 Palladium–DPPP-catalysed homocoupling of organosilanes[a]

Entry	Organosilane	Time (h)	Yield (%)[b]	Product
1	**1a**	12	69	**2a**
2	**1b**	12	57	**2b**
3	**1c**	12	50	**2c**
4	**1d**	24	70	**2d**
5	**1e**	12	94	**2e**
6	**1f**	24	90	**2f**
7	**1g**	24	86	**2g**
8	**1h**	24	70	**2h**
9	**1i**	24	11	**2i**
10	**1j**	18	80	**2j**
11	**1k**	24	77	**2k**
12	**1l**	24	78	**2l**
13	**1m**	30	85	**2m**
14	**1n**	24	86	**2n**
15	**1o**	24	30	**2o**
16	**1p**	24	55	**2p**
17	**1q**	48	33	**2q**
18	**1r**	12	87	**2r**
19	**1s**	24	80	**2s**

[a] The reaction was carried out in DMSO at 70 °C (alkynylsilane) or DMSO/H_2O at 100 °C (arylsilane). See ESI† for details. [b] Isolated yield based on **1**.



Scheme 2 Plausible catalytic cycles of the homocoupling.

In conclusion, we have developed the palladium–DPPP complex-catalysed activator-free oxidative homocoupling reaction of organosilanes. Further studies on details of the mechanism as well as application of the present catalytic system to other activator-free carbon–carbon bond forming reactions of organosilanes are in progress.

Notes and references

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4 Although this reaction proceeds smoothly without an aid of an activator in the presence of a stoichiometric amount of $Pd(OAc)_2$, addition of $Cu(OAc)_2$ and LiOAc is essential for the successful catalytic reaction: (*a*) K. Hirabayashi, J.-i. Ando, J. Kawashima, Y. Nishihara, A. Mori and T. Hiyama, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 1409; (*b*) K. Hirabayashi, Y. Nishihara, A. Mori and T. Hiyama, *Tetrahedron Lett.*, 1998, **39**, 7893.

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6 We have already reported the palladium–DPPP-catalysed base-free oxidative homocoupling of arylboronic esters: H. Yoshida, Y. Yamaryo, J. Ohshita and A. Kunai, *Tetrahedron Lett.*, 2003, **44**, 1541.

7 In the absence of water, the reaction of **1d** gave only a 40% yield of **2d** along with disiloxane, $(PhMe_2Si)_2O$, that cannot participate in the homocoupling. Thus we consider that the addition of water would inhibit the dehydrative condensation of silanols into disiloxanes.

8 (*a*) J. E. Lyons, in *Oxygen Complexes and Oxygen Activation by Transition Metals*, ed. A. E. Martell and D. T. Sawyer, Plenum Press, New York, 1988, pp. 233–251; (*b*) S. S. Stahl, J. L. Thorman, R. C. Nelson and M. A. Kozee, *J. Am. Chem. Soc.*, 2001, **123**, 7188; (*c*) B. A. Steinhoff, S. R. Fix and S. S. Stahl, *J. Am. Chem. Soc.*, 2002, **124**, 766.

9 Transmetalation of an organosilanol to palladium(II) acetate without an aid of an activator has been proposed as a key step in the Mizoroki–Heck type reaction, see ref. 4.

10 A referee kindly suggested the possibility of this catalytic cycle.

11 The coordination of a polar solvent to a silicon atom was also considered to be necessary for the smooth transmetalation of organosilanes to a copper(I) salt, see ref. 2*d* and 5*c*.