


 Cite this: *RSC Adv.*, 2019, **9**, 17425

 Received 17th April 2019
 Accepted 28th May 2019

 DOI: 10.1039/c9ra02895a
rsc.li/rsc-advances

Dimethylformamide-stabilised palladium nanoclusters catalysed coupling reactions of aryl halides with hydrosilanes/disilanes†

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N,N-Dimethylformamide-stabilised Pd nanocluster (NC) catalysed cross-coupling reactions of hydrosilane/disilane have been investigated. In this reaction, the coupling reaction proceeds without ligands with low catalyst loading. *N,N*-Dimethylacetamide is a crucial solvent in these reactions. The solvent effect was considered by various techniques, such as transmission electron microscopy, X-ray photoelectron spectroscopy, and thermogravimetric analysis. The Pd NCs can be recycled five times under both hydrosilane and disilane reaction conditions.

Introduction

Arylsilanes have attracted a great deal of interest in various fields. Silicon-containing molecules have unique and specific properties and various uses, such as in medicine,¹ in photonics,² and as organic intermediates.³ Conventional methods for arylsilane synthesis are unsatisfactory because of byproducts and side reactions.⁴ Accordingly, considerable attention has focused on their selective synthesis.⁵ Transition metal catalysed cross-coupling reactions between aryl halides and hydrosilanes or disilanes have emerged as selective and easy to handle protocols. However, these reactions are generally achieved using transition metal complexes, such as Pd⁶ and Rh⁷ complexes, with 1–5 mol% of the catalyst. In addition, hydrosilanes act as weak reducing reagents⁸ and using them as coupling substrates inhibits reduction of aryl halides. Moreover, owing to the stability of the Si–Si bond, disilanes show low reactivity for silylation reagents, so the coupling reactions require bulky phosphorus ligands.⁹

Metal nanoparticles (NPs) and nanoclusters (NCs) have unique physical and chemical properties.¹⁰ They are expected to show high catalytic performance owing to their stability, selectivity, activity, and recyclability.^{11,12} On the other hand, colloidal nanocatalysts require removal of capping agent to access catalytically active surface. Stabilizing agents such as thiolates, phosphines, surfactants, and polymers, behaves a protect shell

for reactant.¹³ We have reported a surfactant-free preparation of dimethylformamide (DMF)-stabilised transition-metal (Au, Fe, Ir, Cu, and Pd) NPs by the DMF reduction method.¹⁴ Among these NPs, Pd NCs have proven to be highly effective in various palladium-catalysed cross-coupling reactions, such as Suzuki–Miyaura, Mizoroki–Heck,^{15a} and Migita–Kosugi–Stille coupling reactions.^{15b} DMF-stabilised Fe₂O₃ NPs also show high catalytic activity for hydrosilylation of unactivated terminal alkenes.¹⁶ The Pd–Pt–Fe₂O₃ nanocatalyst has recently been reported for coupling aryl halides with hydrosilanes. However, the Pd monometallic catalyst shows low reactivity and causes decomposition.¹⁷

In this paper, we describe DMF-stabilised palladium NCs catalysed coupling reactions of aryl halides with hydrosilanes/disilanes to give arylsilanes with moderate to good yields. These reactions proceed at low catalyst loading under ligand and additive free conditions. In addition, the Pd NCs catalysts in both the hydrosilane/disilane reaction systems can be recycled at least five times.

Results and discussion

Initially, we chose to study the cross-coupling reaction between iodobenzene (**1a**) and dimethylphenylsilane (**2a**) using LiOAc as a base in DMF at 100 °C. After 16 h, dimethyldiphenylsilane (**3a**) was obtained in moderate yield (Table 1, entry 1). When we changed *N*-dimethylacetamide (DMAc) solvent to the reaction, the yield increased to 80% (entry 2). The reaction was achieved by using low Pd loadings compared with the previously reported catalytic processes.^{6b,d} During the course of the reaction, small amount of benzene (<10% yield) was observed as byproduct. The reaction was not accelerated in *N*-methyl-2-pyrrolidone (NMP) and toluene (entries 3 and 4). Various bases were tested. LiOAc gave the highest yield (entries 5–6). The use of

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† Electronic supplementary information (ESI) available: Characterization and spectra. See DOI: [10.1039/c9ra02895a](https://doi.org/10.1039/c9ra02895a)



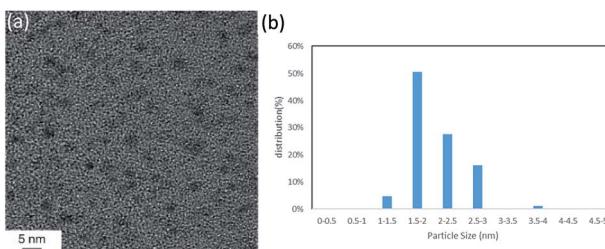
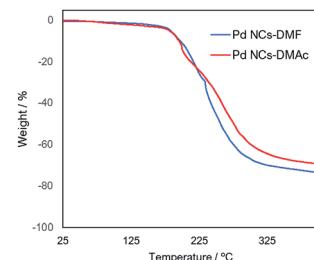
Table 1 Optimisation of the coupling reaction conditions with hydrosilane^a

Entry	Solvent	Base	Conv. (%)	Yield ^b (%)	<chem>Ic1ccccc1 + HSiPhMe2 ->[catalyst] Pd NCs (0.1 mol %) + Base (1 equiv) + Solvent (1 mL), 100 °C, 16 h 3a</chem>		
					1a	2a	3a
1	DMF	LiOAc	>99	52			
2	DMAc	LiOAc	>99	80 (75)			
3	NMP	LiOAc	— ^c	41			
4	Toluene	LiOAc	66	7			
5	DMAc	NaOAc	>99	68			
6	DMAc	KOAc	>99	57			
7	DMAc	KOtBu	>99	8			
8	DMAc	None	>99	52			
9 ^d	DMAc	LiOAc	97	9			

^a Reaction conditions: **1a** (1.0 mmol), **2a** (3.0 mmol), Pd NCs (0.1 mol%), and base (1.0 mmol) in solvent (1.0 mL) at 100 °C for 16 h. ^b The conversion of **1a** and yields were determined by gas chromatography (GC) analysis. The isolated yield is shown in parenthesis. ^c Not determined due to overlapping of GC peaks. ^d PdCl₂ was used as catalyst precursor.

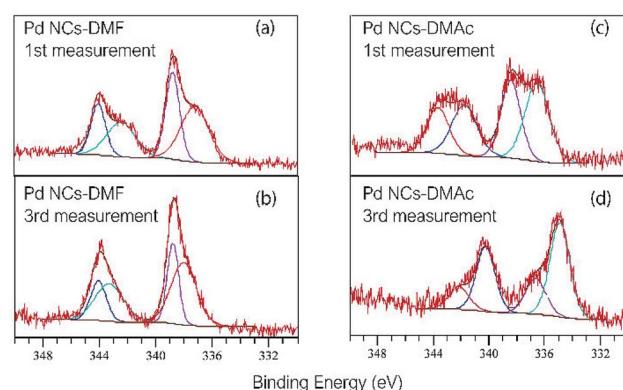
KOtBu under these conditions gave the product in 8% yield along with intractable byproduct (by GC) (entry 7). The reaction also occurred in the absence of a base (entry 8). The use of PdCl₂ under these conditions shows low catalytic activity (entry 9). To investigate the specific solvent effect, we prepared Pd NCs in DMF followed by a replacement of DMF on the Pd NCs by using DMAc by heating at 100 °C for 24 h. A TEM image and the particle size distribution of the DMAc-displaced Pd NCs are shown in Fig. 1. The average particle size of 2 nm is the same as that of the prepared Pd NCs (Fig. 1).

¹H-NMR spectroscopy, Fourier transform-infrared (FT-IR) spectroscopy, thermogravimetric (TG) analysis, and X-ray photoelectron spectroscopy (XPS) were performed to analyse the DMAc-substituted Pd NCs. From ¹H-NMR analysis, several peaks around 8 ppm in ¹H-NMR assigned to formyl protons of DMF molecules on the Pd NCs.^{14f,15a–c} The formyl group proton (δ = 8.14 ppm) disappears after solvent displacement (Fig. S1†). FT-IR analysis (Fig. S2†) shows a peak at 1670 cm^{–1}, which is attributed to the *n*(C=O) stretching vibration and indicates the presence of DMF and DMAc molecules. The thermal stability of the Pd NPs was investigated by TG analysis (Fig. 2). The TG

**Fig. 1** (a) TEM image (scale bar = 5 nm) and (b) nanoparticle size distribution of the DMAc-displaced Pd NCs.**Fig. 2** TG analysis of Pd NCs-DMF (blue) and Pd NCs-DMAc (red).

curves in the range of 25 °C to 200 °C of the two Pd NCs-prepared by DMF (Pd NCs-DMF) and the Pd NCs covered by DMAc (Pd NCs-DMAc) indicated similar charts. A difference was observed in the TG curves of the both Pd nanoclusters from above 200 °C, suggesting that the two nanoparticles were protected by different molecules on the surface on the metal clusters (DMF and DMAc).

The surface states of the as-prepared Pd NCs and solvent-displaced Pd NCs with DMAc were determined by XPS. The binding energy positions of Pd 3d_{5/2} and Pd 3d_{3/2} are shown in Fig. 3. Peak FWHMs are described in Table S1.† The other main peaks (C, O, and N) are shown in Fig. S4–S6.† The main peaks of Pd at 338.8, 337.2 eV of 3d_{5/2} and 344.0, 342.1 of 3d_{3/2} was higher than that of bulk Pd (Pd 3d_{5/2} 335.1 eV and Pd 3d_{3/2} 340.3 eV).^{18,19} The Pd 3d_{5/2} and 3d_{3/2} spectrum of Pd NCs with DMF is shown in Fig. 3a. The DMAc Pd NCs have a broad peak (Pd 3d_{5/2} 343.7, 341.8 eV and Pd 3d_{3/2} 338.5, 336.6 eV) (Fig. 3b). A significant peak shift in Pd NCs with DMAc by increase of the measurement time (Fig. 3d). In contrast, the as-prepared Pd NCs remain unchanged (Fig. 3c). The changes in the two samples are caused by removal of the protective molecules on the surface. With irradiation by X-ray and sample heating, the protective molecules (DMF rigid protecting layer) are removed as the number of measurements increases. With elimination of the protective surface molecules, surface palladium is reduced. These data are associated with the TG analysis results, where DMAc displacement of the Pd NCs removes the capping molecules and results in easy access to the active sites.

**Fig. 3** XPS spectra of Pd NCs with DMF (a) at first measurement, (b) at third measurement, and Pd NCs with DMAc which substituted from DMF (c) at 1st and (d) at 3rd measurement.

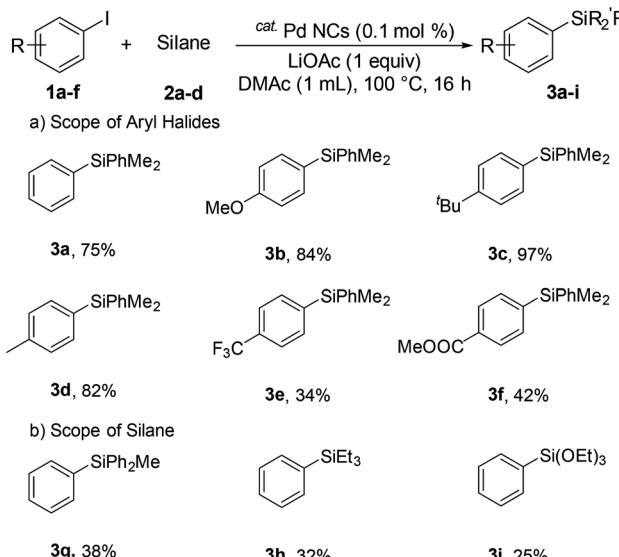
Next, we investigated aryl halides bearing both electron-donating and electron-withdrawing substituents (Scheme 1). Electron-donating substrates (4-methyl and 4-methoxy, and 4-*tert*-butyl) gave excellent yields (84%, 97%, and 82% for **3b**, **3c**, and **3d**, respectively). Electron withdrawing substrates were less effective (34% and 42% for **3e** and **3f**, respectively). Various silanes were investigated. The corresponding arylsilanes diphenylmethylsilane (**3g**), triethylsilane (**3h**), and triethoxysilane (**3i**) were obtained in 38%, 32%, and 25% yield, respectively.

We wanted to extend the coupling reaction to disilanes. Hexamethyldisilane is readily available as a Rochow direct process byproduct.²⁰ The reaction of iodobenzene with hexamethyldisilane at 120 °C afforded **5a** in 70% yield (Table 2, entry 1). Various bases were examined. NaOAc showed the best performance (entries 2–5). The same solvent effect was observed for DMF and DMAc (entry 6). The presence of a base was necessary for the reaction (entry 7). The reaction by using PdCl₂ as catalyst precursor and gave the product in 38% (entry 8).

Iodobenzene derivatives bearing electron-donating groups, such as *p*-methyl, *p*-methoxy, and *p*-*tert*-butyl groups, gave the corresponding products in good yields (Table 3, entries 2–4). Electron-withdrawing groups were less effective (entries 5–7). However, the reaction of bromo/chlorobenzene under these conditions was sluggish.

Based on the results and those reported in the literature, the plausible reaction mechanisms are shown in Scheme S7.^{†21} Iodobenzene or hydrosilane oxidatively adds to the Pd NCs. The desired coupling product is obtained by the σ -bond metathesis reaction.

We investigated possible reuse of the catalyst.²² After the reaction, we performed annular dark field scanning transmission electron microscopy (ADF-STEM) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis (Table S2[†]). The particle size remained the same (Fig. 4).



Scheme 1 Scope of various substrates.

Table 2 Optimisation of the arylsilylation condition with hexamethyldisilane^a

Entry	Solvent	Base	Conv. (%)	Yield ^b (%)
1	DMAc	LiOAc	>99	70
2	DMAc	NaOAc	>99	83 (70)
3	DMAc	KF	>99	73
4	DMAc	Na ₂ CO ₃	>99	78
5	DMAc	KOtBu	89	27
6	DMF	NaOAc	>99	69
7	DMAc	None	58	32
8 ^c	DMAc	NaOAc	78	38

^a Reaction conditions: **1a** (1.0 mmol), **4** (3.0 mmol), Pd NCs (0.1 mol %), and base (1.0 mmol) in solvent (1.0 mL) at 120 °C for 24 h. ^b The conversion of **1a** and yields were determined by GC analysis. The isolated yield is shown in parenthesis. ^c PdCl₂ was used as catalyst precursor.

Based on a previous study, the results suggest that the Pd NCs possess recyclability in the coupling reaction.

We investigated the recyclability of the Pd NCs (Fig. 5 and 6). After performing the reaction with the disilane system (Table 2, entry 2), the hexane layer was extracted using 8 mL of hexane five times. The hexane layer (containing the starting materials and products) was removed. The DMAc was evaporated from the residual DMAc layer containing Pd NCs and the residue was reused as the catalyst for the reaction under the same conditions (Table 2, entry 2). The Pd NCs gave good yields five times. We also tested the coupling reaction of aryl halide with hydrosilane (reaction conditions as in Table 1, entry 2). In the hydrosilane coupling reaction, the extraction solvent was modified. Product **3a** and the starting materials were extracted using a mixed solvent (hexane : ethyl acetate = 95 : 5). The Pd NCs catalyst tolerated multiple cycles.

Table 3 Coupling Reaction of Aryl halides **1a** with hexamethyldisilane^a

Entry	X	R	Product	Yield ^b (%)
1	I	H	5a	70
2		<i>p</i> -Me	5b	65
3		<i>p</i> -OMe	5c	73
4		<i>p</i> - <i>t</i> Bu	5d	86
5		<i>p</i> -COMe	5e	66
6		<i>p</i> -COOMe	5f	59
7		<i>p</i> -CF ₃	5g	48
8	Br	H	5a	5 ^c
9	Cl	H	5a	Trace ^c

^a Reaction conditions: **1a** (1.0 mmol), **2a** (3.0 mmol), Pd NCs (0.1 mol %), and base (1.0 mmol) in DMAc (1.0 mL) at 120 °C for 24 h. ^b Isolated yield. ^c GC yield.



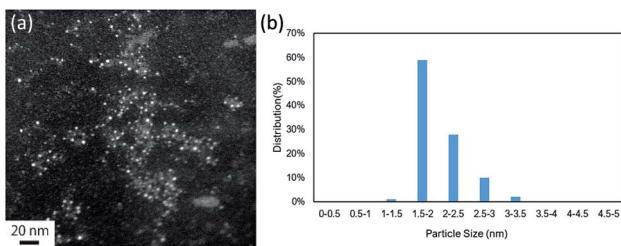


Fig. 4 (a) ADF-STEM image (scale bar = 20 nm) and (b) particle size distribution of the Pd NCs after the reaction.

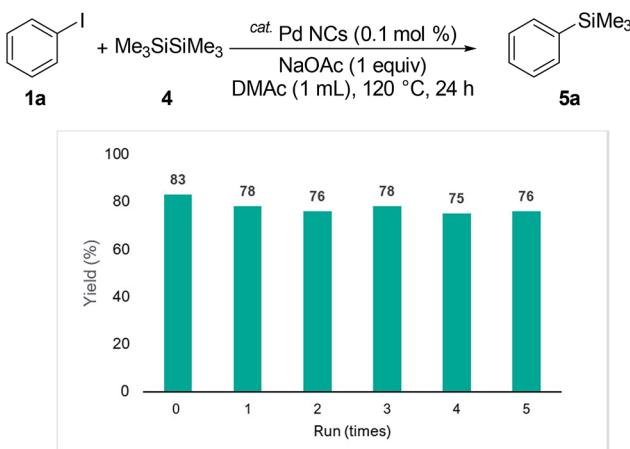


Fig. 5 Multiple catalyst recycling for coupling of iodobenzene with disilane (conditions as in Table 2, entry 2).

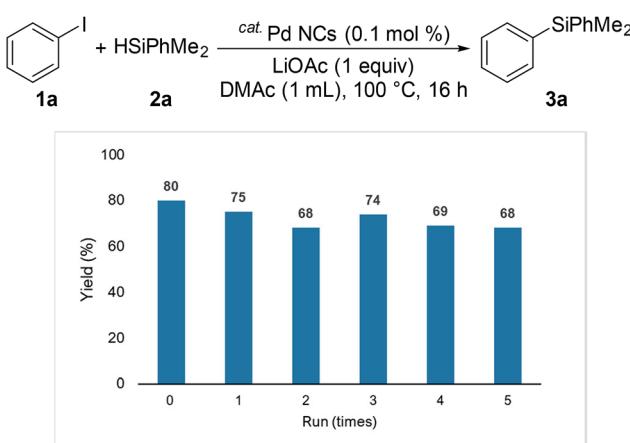


Fig. 6 Multiple catalyst recycling for coupling of iodobenzene with hydrosilane (conditions as in Table 1, entry 2).

Conclusions

We have developed Pd NCs catalytic system for silylation of aryl halides with hydrosilanes. The Pd NCs catalyst can be separated and reused at least five times without notable loss of the catalytic activity. The same catalyst can also be used for silylation of hexamethyldisilane. DMAc displacement enables easy access to the active sites of the Pd NCs. Further investigation of metal NPs as catalysts is underway.

Experimental

1. General

GC analysis was performed with a flame ionisation detector using a 0.22 mm × 25 m capillary column (BP-5). The ¹H and ¹³C NMR spectra were recorded at 400 and 100 MHz, respectively. The ¹H and ¹³C NMR chemical shifts are reported in ppm with respect to the residual chloroform (¹H 7.26 ppm, ¹³C 77 ppm). The products were characterised by ¹H NMR, ¹³C NMR, and GC-MS. The TEM and STEM images were obtained with a JEOL JEM-ARM200F instrument at an accelerating voltage of 200 kV. Size distributions of nanoparticles were measured by counting 100 nanoparticles. ICP-AES was performed with a Shimadzu ICPS-8100 spectrometer. XPS analysis was performed with a ULVAC-PHI PHI5000 VersaProbe with Al K α radiation. The measured spectra were calibrated by the C 1 s electron peak (284.5 eV). TG analysis was performed with a Thermo Plus EVO device (Rigaku, Japan) at a heating rate of 10 °C min⁻¹ under nitrogen flow.

All of the synthesised compounds (**3a**,^{23a} **3b**,^{23a} **3c**,^{23a} **3d**,^{23b} **3e**,^{23a} **3f**,^{23b} **3g**,^{23e} **3h**,^{23c} **3i**,^{23d} **5a**,^{24a} **5b**,^{24c} **5c**,^{24c} **5d**,^{24b} **5e**,^{24b} **5f**,^{24d} and **5g**,^{24b}) are known compounds and have been previously reported.

All of the starting materials were commercially available and used without further purification. The DMF-protected Pd NCs were prepared according to a previously reported method.^{15a}

(A) Preparation of the DMF-stabilised Pd NCs. DMF (50 mL) was added to a 300 mL three-necked round bottom flask. The solution was preheated to 140 °C (±2 °C) and stirred at 1500 rpm for 5 min. PdCl₂ solution (0.1 M, 500 μ L) was then added to the hot DMF solution, which was allowed to react for 10 h under stirring (1500 rpm) at 140 °C (±2 °C). The resulting clear yellow solution was used as the 1 mM Pd NCs solution in DMF. In prior to the catalytic reaction, DMF solvent was removed *in vacuo*, then the residue was dissolved in DMAc (50 mL) and stirred the reaction mixture at 100 °C for 24 h. Subsequent solvent evaporation *in vacuo* and the residue was used as Pd NCs-DMAc for the measurements and coupling reaction.

2. Typical procedure

(A) Reaction of aryl halides with hydrosilanes. A mixture of iodobenzene (**1a**, 204 mg, 1 mmol), dimethylphenylsilane (**2a**, 409 mg, 3 mmol), LiOAc (67 mg, 1 mmol), Pd NCs in DMAc (1 mL, 1 mM) as a catalyst, and solvent was stirred at 100 °C for 16 h in an Ar atmosphere. The product and substrate conversions and yields were estimated by GC from the peak areas based on an internal standard (*n*-decane). **3a** was obtained in 80% yield. **3a** was isolated by column chromatography [silica gel (230–400 mesh), *n*-hexane as eluent] in 75% yield (159 mg).

3a dimethyldiphenylsilane: colorless liquid, ¹H-NMR (400 MHz; CDCl₃; CDCl₃) δ : 7.57–7.54 (4H, m, Ph), 7.39–7.38 (6H, m, Ph), 0.59 (6H, s, Me); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ : 138.22 (C) 134.22 (CH), 129.11 (CH), 127.82 (CH), –2.42 (CH₃); GC-MS (EI) *m/z* (relative intensity) 212(23) [M]⁺, 197(100), 198(19), 105(9).



3b dimethyl(phenyl)(*p*-tolyl)silane: colorless liquid, ¹H-NMR (400 MHz; CDCl₃; CDCl₃) δ : 7.57–7.55 (2H, m, Ph), 7.48–7.46 (2H, m), 7.39–7.38 (3H, m, Ph), 7.23–7.21 (2H, m, Ph), 2.39 (3H, s, SiMe₂), 0.58 (6H, s, Me); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ : 138.96 (C), 138.50 (C), 134.53 (C), 134.23 (CH), 134.15 (CH), 129.00 (CH), 128.65 (CH), 127.76 (CH), 21.45 (CH₃), –2.32 (CH₃); GC-MS (EI) *m/z* (relative intensity) 226(18) [M]⁺, 211(100), 212(21), 105(7).

3c (4-ethoxyphenyl)dimethyl(phenyl)silane: colorless liquid, ¹H-NMR (400 MHz; CDCl₃; CDCl₃) δ : 7.53–7.44 (7H, m, Ph), 6.97–6.95 (2H, m, Ph), 3.85 (3H, s, OMe), 0.58 (6H, s, SiMe₂); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ : 160.48 (C), 138.66 (C), 135.62 (CH), 134.11 (CH), 128.97 (CH), 127.75 (CH), 113.58 (CH), 54.97 (CH₃), –2.32 (CH₃); GC-MS (EI) *m/z* (relative intensity) 242(20) [M]⁺, 227(100), 135(4).

3d (4-(*tert*-butyl)phenyl)dimethyl(phenyl)silane: colorless liquid, ¹H-NMR (400 MHz; CDCl₃; CDCl₃) δ : 7.21–7.01 (9H, m, Ph), 0.98 (9H, s, *t*Bu), 0.21 (6H, s, SiMe₂); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ : 151.98 (C), 138.46 (C), 134.59 (C), 134.15 (CH), 134.04 (CH), 128.99 (CH), 127.75 (CH), 124.77 (CH), 34.62 (C), 31.22 (CH₃), –2.34 (CH₃); GC-MS (EI) *m/z* (relative intensity) 268(16) [M]⁺, 253(100), 237(6), 105(10).

3e dimethyl(phenyl)(4-(trifluoromethyl)phenyl)silane: ¹H-NMR (400 MHz; CDCl₃; CDCl₃) δ : 7.64–7.61 (4H, m, Ph), 7.53–7.52 (2H, m, Ph), 7.41–7.38 (3H, m Ph), 0.60 (6H, s, SiMe₂); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ : 143.36 (q, ⁴J_{C-F} = 1.0 Hz, CH), 137.03 (CH), 134.41 (CH), 134.10 (CH), 130.99 (q, ²J_{C-F} = 32.2 Hz, CH), 129.45 (CH), 127.97 (CH), 124.29 (q, ³J_{C-F} = 3.7 Hz, CH), 124.19 (q, ¹J_{C-F} = 273.0 Hz, C), –2.63 (CH₃); GC-MS (EI) *m/z* (relative intensity) 280(4) [M]⁺, 265(100), 184(15).

3f methyl 4-(dimethyl(phenyl)silyl)benzoate: colorless liquid, ¹H-NMR (400 MHz; CDCl₃; CDCl₃) δ : 8.00 (2H, dd, *J* = 8.3, 0.7 Hz, Ph), 7.60 (2H, dd, *J* = 8.3, 0.7 Hz, Ph), 7.51–7.49 (2H, m, Ph), 7.38–7.37 (3H, m, Ph), 3.92 (3H, s, OMe), 0.58 (6H, d, *J* = 0.6 Hz, SiMe₂); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ : 167.22 (C), 144.63 (C), 137.28 (C), 134.13 (CH), 134.11 (CH), 130.49 (C), 129.34 (CH), 128.51 (CH), 127.91 (CH), 52.12 (CH₃), –2.61 (CH₃); GC-MS (EI) *m/z* (relative intensity) 270(7) [M]⁺, 256(20), 255(100), 239(2).

3g methyltriphenylsilane: colorless liquid, ¹H-NMR (400 MHz; CDCl₃; CDCl₃) δ : 7.56–7.36 (15H, m, Ph), 0.87 (3H, s, SiMe); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ : 136.06 (C), 135.25 (CH), 129.37 (CH), 127.83 (CH), –3.40 (CH₃); GC-MS (EI) *m/z* (relative intensity) 274(5) [M]⁺, 259(100), 180(12).

3h triethyl(phenyl)silane: colorless liquid, ¹H NMR (400 MHz; CDCl₃; CDCl₃) δ 7.50–7.35 (m, 2H, Ph), 7.34–7.25 (m, 3H, Ph), 0.96 (t, *J* = 8.0 Hz, 9H, Me), 0.79 (q, *J* = 7.2 Hz, 6H, SiCH₂); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ 137.8 (C), 134.5 (CH), 129.0 (CH), 127.9 (CH), 7.7 (CH₃), 3.6 (CH₂); GC-MS (EI) *m/z* (relative intensity) 192(6) [M]⁺, 163(59), 135(100), 107(77).

3i triethoxy(phenyl)silane: colorless liquid, ¹H NMR (400 MHz; CDCl₃; CDCl₃) δ 7.68 (d, *J* = 6.4 Hz, 2H, Ph), 7.34 (m, 3H, Ph), 3.87 (q, *J* = 7.2, 6H, OCH₂), 1.25 (t, *J* = 6.8 9H, Me); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ 134.8 (C), 130.9 (CH), 130.4 (CH), 127.9 (CH), 58.7 (CH₂), 18.2 (CH₃); GC-MS (EI) *m/z* (relative intensity) 240(23) [M]⁺, 195(42), 145(100), 135(36).

(B) Reaction of aryl halides with disilanes. A mixture of iodobenzene (**1a**, 204 mg, 1 mmol), hexamethyldisilane (**4**, 439 mg, 3 mmol), NaOAc (82 mg, 1.0 mmol), and Pd NCs in DMAc (1.0 mL, 1 mM) as a catalyst was stirred at 120 °C for 24 h in an Ar atmosphere. Conversion of the substrate and the yield of the product were estimated by GC from the peak areas based on an internal standard (*n*-tridecane). **5a** was obtained in 83%. **5a** was isolated by column chromatography [silica gel (230–400 mesh), petroleum ether as eluent] in 70% yield (105 mg), ¹H NMR (400 MHz; CDCl₃; CDCl₃) 7.66–7.46 (2H, m, Ph), 7.40–7.33 (3H, m, Ph), 0.27 (9H, s, SiMe₃); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ : 140.47 (C), 133.28 (CH), 128.75 (CH), 127.71 (CH), –1.16 (CH₃); GC-MS (EI) *m/z* (relative intensity) 150(18) [M]⁺, 136(12), 135(100).

5b trimethyl(*p*-tolyl)silane: colorless liquid, ¹H-NMR (400 MHz; CDCl₃; CDCl₃) δ 7.45 (d, *J* = 8.0 Hz, 2H, Ph), 7.20 (d, *J* = 7.6 Hz, 2H, Ph), 2.37 (s, 3H, Me), 0.27 (s, 9H, SiMe₃); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ 138.6 (C), 136.8 (C), 133.3 (CH), 128.6 (CH), 21.5 (CH₃), –1.1 (CH₃); GC-MS (EI) *m/z* (relative intensity) 164(13) [M]⁺, 149(100), 121(9).

5c (4-methoxyphenyl)trimethylsilane: colorless liquid, ¹H-NMR (400 MHz; CDCl₃; CDCl₃) δ 7.20 (d, *J* = 8.8 Hz, 2H, Ph), 6.67 (d, *J* = 8.4 Hz, 2H, Ph), 3.56 (s, 3H, OMe), 0.00 (s, 9H, SiMe₃); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ 162.2 (C), 135.7 (CH), 132.2 (C), 114.4 (CH), 55.9 (CH₃), 0.00 (CH₃); GC-MS (EI) *m/z* (relative intensity) 180(16) [M]⁺, 165(100), 135(9).

5d (4-(*tert*-butyl)phenyl)trimethylsilane: white solid, m.p. 77.5–78, ¹H-NMR (400 MHz; CDCl₃; CDCl₃) δ 7.49 (d, *J* = 8.4 Hz, 2H, Ph), 7.41 (d, *J* = 8.0 Hz, 2H, Ph), 1.34 (s, 9H, Me), 0.27 (s, 9H, SiMe₃); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ 151.7 (C), 136.9 (C), 133.2 (CH), 124.7 (CH), 34.6 (C), 31.2 (CH₃), –1.06(CH₃); GC-MS (EI) *m/z* (relative intensity) 206(12) [M]⁺, 191(100), 176(7).

5e 1-(4-(trimethylsilyl)phenyl)ethan-1-one: colorless liquid, ¹H-NMR (400 MHz; CDCl₃; CDCl₃) δ : 7.92–7.91 (2H, m, Ph), 7.63–7.61 (2H, m, Ph), 2.60 (3H, s, COMe), 0.29 (9H, s, SiMe₃); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ : 198.33 (C), 147.21 (C), 137.17 (C), 133.48 (CH), 127.19 (CH), 26.58 (CH₃), –1.38 (SiMe₃); GC-MS (EI) *m/z* (relative intensity) 192(14) [M]⁺, 177(100), 162(1), 119(7).

5f methyl 4-(trimethylsilyl)benzoate: colorless liquid, ¹H-NMR (400 MHz; CDCl₃; CDCl₃) δ : 7.99 (2H, d, *J* = 8.3 Hz, Ph), 7.59 (2H, d, *J* = 8.2 Hz, Ph), 3.92 (3H, s, OMe), 0.29 (9H, s, SiMe₃); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ : 167.28 (C), 146.84 (C), 133.27 (CH, s), 130.19 (C), 128.44 (CH), 52.09 (CH₃), –1.34 (CH₃); GC-MS (EI) *m/z* (relative intensity) 208(5) [M]⁺, 193(100), 133(14).

5g trimethyl(4-(trifluoromethyl)phenyl)silane: ¹H-NMR (400 MHz, CDCl₃; CDCl₃) δ 7.64 (d, *J* = 7.6 Hz, 2H, Ph), 7.59 (d, *J* = 8.0 Hz, 2H, Ph), 0.30 (s, 9H, SiMe₃); ¹³C-NMR (100 MHz; CDCl₃; CDCl₃) δ 145.6 (C), 133.8 (CH), 130.8 (q, *J* = 31.6 Hz, C), 124.3 (q, *J* = 270.2 Hz, C), 124.2 (q, *J* = 3.9 Hz CH), –1.41(CH₃); GC-MS (EI) *m/z* (relative intensity) 218(6) [M]⁺, 203(100), 189(0.60).

3. Preparation of the TEM sample

(A) Pd NCs-DMAc (before the reaction). After preparation the Pd NCs, Solvent DMF was displaced DMAc. The DMAc Pd



NCs solution was stirred at 100 °C, 24 h, then they were diluted with 3 mL of ethanol and added dropwise onto the TEM grid (Cu).

(B) **Pd NCs-DMAc (after the reaction).** After the reaction under the conditions given in Table 2, entry 2, the reaction mixture was extracted with a mixed solvent [hexane : ethyl acetate (99 : 1), 5 mL, 5 times] to remove **5a**. DMAc was removed by evaporation under high vacuum and then redispersed in ethanol.

4. Recycling experiment

(A) **Reaction of aryl halides with hydrosilanes.** The Pd NCs were separated from **3a** using a mixed solvent (hexane : ethyl acetate = 95 : 5, 5 mL, ten times, upper phase containing **3a**). The Pd NCs remained in the DMAc solvent (bottom phase). Conversion of the substrate and the yield of the product were calculated from their GC peak areas based on an internal standard (*n*-decane). The DMAc solution containing the Pd NCs was filtered through a cotton plug to remove the Pd NCs from the DMAc solution. DMAc was removed under vacuum and the residue was redissolved in DMAc (1 mL). Pd NCs in DMF were used for the next catalytic reaction under the reaction conditions given in Table 1, entry 2 by adding iodobenzene (**1a**, 109 mg, 1.0 mmol), dimethylphenylsilane (**2a**, 409 mg, 3.0 mmol), and LiOAc (67 mg, 1.0 mmol).

(B) **Reaction of aryl halides with disilanes.** The Pd NCs were separated from **5a** using hexane (5 mL, ten times). The upper phase contained **5a**. The Pd NCs remained in the DMAc solvent (bottom phase). Conversion of the substrate and the yield of the product were calculated from their GC peak areas based on an internal standard (*n*-tridecane). The DMAc solution containing the Pd NCs was filtered through a cotton plug to remove the Pd NCs from the DMAc solution. DMAc was removed under vacuum and the residue was redissolved in DMAc (1 mL). The Pd NCs in DMAc were used for the next catalytic reaction under the reaction conditions given in Table 2, entry 2 by adding iodobenzene (**1a**, 204 mg, 1.0 mmol), hexamethyldisilane (**4**, 409 mg, 3.0 mmol), and NaOAc (82 mg, 1.0 mmol).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the “Development of Innovative Catalytic Processes for Organosilicon Functional Materials” project (PL: K. Sato, AIST) from the New Energy and Industrial Technology Development Organization (NEDO). We thank the members of the Comprehensive Analysis Center, SANKEN (ISIR), Osaka University, for TEM, ICP-AES analyses.

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