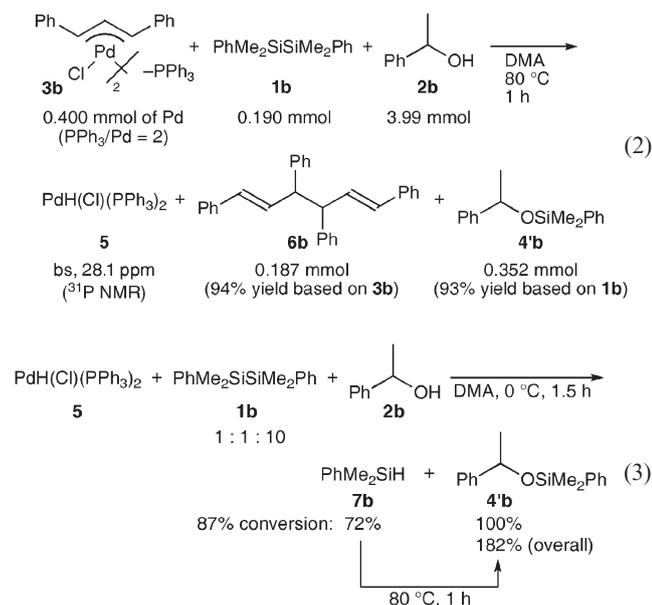
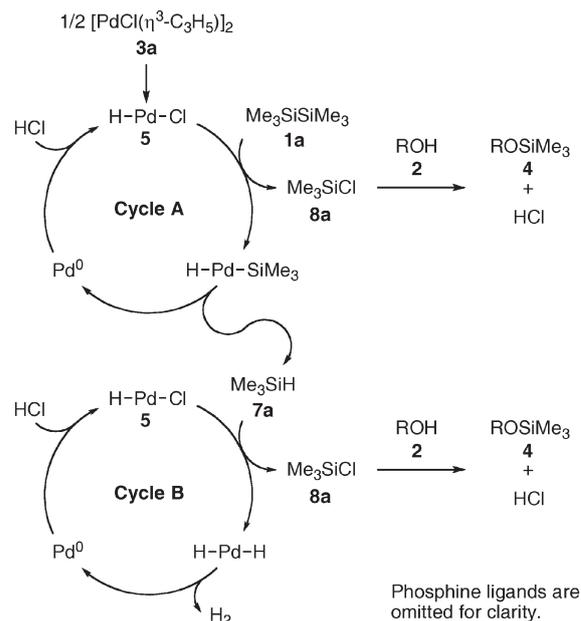


and 1,1,2,2-tetramethyl-1,2-diphenyldisilane (**1b**) instead of $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$ (**3a**) and **1a**, where phenyl substituents facilitate the tracking of the allyl and the silyl moieties. On treatment of **3b** (0.400 mmol of Pd) and PPh_3 (0.800 mmol) with **1b** (0.190 mmol) in the presence of 1-phenylethanol (**2b**: 3.99 mmol) in DMA at 80 °C for 1 h, we observed the formation of $\text{PdH}(\text{Cl})(\text{PPh}_3)_2$ (**5**), which was confirmed by ^{31}P NMR (bs, 28.1 ppm).⁸ The reaction mixture was analyzed by GC, and was found to contain 1,3,4,6-tetraphenyl-1,5-hexadiene (**6b** as a mixture of diastereomers: 0.187 mmol, 94% yield based on **3b**) and 1-[dimethyl(phenyl)siloxy]-1-phenylethane (**4'b**: 0.352 mmol, 93% yield based on **1b**) (eqn (2)).⁹ $\text{PdH}(\text{Cl})(\text{PPh}_3)_2$ (**5**) thus generated was found to catalyze the trimethylsilylation of **2b** faster than **3a**- PPh_3 (1 : 2): the reaction completed within 1 h under the same conditions as entry 2 of Table 1 to give **4b** in 94% yield.¹⁰ It is interesting that the two silyl groups of **1b** were used for the silylation of alcohol during the conversion of π -allylpalladium **3b** into active H-Pd-Cl complex **5**.



Next, we examined how the silyl groups of disilanes are transferred to alcohols under the influence of $\text{PdH}(\text{Cl})(\text{PPh}_3)_2$ (**5**) (eqn (3)). The reaction of $\text{PhMe}_2\text{SiSiMe}_2\text{Ph}$ (**1b**) with **5** (1.0 equiv.) in the presence of alcohol **2b** (10 equiv.) at 0 °C for 1.5 h proceeded with 87% conversion to give **4'b** (100% yield) and PhMe_2SiH (**7b**: 72% yield), which also was efficiently transformed further to **4'b** upon heating at 80 °C for 1 h.^{3,11} Silyl ether **4'b** observed before heating is possibly generated by the reaction of initially formed PhMe_2SiCl (**8b**) with alcohol **2b**. Although we failed to detect **8b** in the reaction mixture of eqn (3) in the absence of **2b** due to its instability in DMA,¹² chlorosilane **8b** (60%) and hydrosilane **7b** (34%) were observed by GC analysis on treatment of **1b** with **5** (1.0 equiv.) in THF at 25 °C for 10 min, with 48% conversion. As chlorosilanes are known to be obtained from hydrosilanes and HCl in the presence of a palladium catalyst,¹³ silyl ether **4'b** derived from hydrosilane **7b** upon heating (eqn (3)) is likely to be produced through chlorosilane **8b** in the presence of H-Pd-Cl complex **5**.

Considering the generation of a chlorosilane and a hydrosilane as the intermediates for silyl ether **4**, catalytic cycles starting with



Scheme 1

H-Pd-Cl **5** with the use of $\text{Me}_3\text{SiSiMe}_3$ (**1a**) and $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$ (**3a**) are likely to be depicted as shown in Scheme 1. In Cycle A, H-Pd-Cl **5** first reacts with **1a** to give H-Pd-SiMe₃ and Me_3SiCl (**8a**), which silylates ROH **2**. Reductive elimination from H-Pd-SiMe₃ gives Me_3SiH (**7a**) and Pd⁰, which accepts oxidative addition of HCl coproduced on the silylation to regenerate H-Pd-Cl **5**. Hydrosilane **7a** thus generated participates in a similar cycle (Cycle B), transmetalating with H-Pd-Cl **5** to give Me_3SiCl (**8a**) and H-Pd-H. The cycle goes along a similar scheme to Cycle A but gives H₂ instead of the hydrosilane.

In conclusion, we have disclosed a new method of trimethylsilylation of alcohols with the aid of a palladium catalyst. The most striking feature is high atom-economy, where H₂ is a sole byproduct in use of just a slightly excess amount of a silyl source.‡

Notes and references

‡ General procedure for the trimethylsilylation of alcohols: To a solution of $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)]_2$ (**3a**: 7.4 mg, 0.040 mmol of Pd) and PPh_3 (21 mg, 0.080 mmol) in DMA (1.0 mL) were added successively an alcohol (**2**: 0.80 mmol) and hexamethyldisilane (**1a**: 70 mg, 0.48 mmol). After stirring at 80 °C for 3 h, the resulting mixture was diluted with diethyl ether (20 mL), washed with water (10 mL × 5) and brine (10 mL), and dried over anhydrous sodium sulfate. After filtration, followed by evaporation of the solvent at atmospheric pressure, the resulting mixture was filtered through an alumina plug (10 mL) using hexane (30 mL) as an eluent. Evaporation of the solvent at atmospheric pressure followed by evacuation at 35 °C under ca. 20 mmHg gave trimethylsilyl ether **4**.

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- 2 For a review, see: E. Lukevics and M. Dzintara, *J. Organomet. Chem.*, 1985, **295**, 265–315.
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- 9 π -Allyl complex **3b** and disilane **1b** were found to be as equally effective as **3a** and **1a**, respectively, as a palladium precursor and a silylating reagent: the reaction of **2b** with **1b** (0.60 equiv.) in the presence of **3b**-PPh₃ (1:2, 5 mol% of Pd) at 80 °C for 3 h gave **4'b** in 92% yield.
- 10 The higher catalytic activity of PdH(Cl)(PPh₃)₂ (**5**) was demonstrated by comparison of the reactions stopped at 10 min: 37% **4b** (**5**) vs. <1% **4b** (**3a**-PPh₃).
- 11 Treatment of **7b** with **5** (1.0 equiv.) and **2b** (10 equiv.) at 80 °C for 1 h gave **4'b** in 89% yield.
- 12 The peak corresponding to **8b** was observed on GC analysis of a THF solution, whereas it was not observed in a DMA solution.
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