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CONVERSION OF DISILANES TO FUNCTIONAL MONOSILANES

XII. * THE PALLADIUM(0)-CATALYZED DECHLORINATIVE SILYLATION OF BENZYLIC CHLORIDES WITH METHYLCHLORODISILANES. A FACILE ROUTE TO BENZYLMETHYLCHLOROSILANES

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Summary

This paper describes the facile dechlorinative silylation of benzylic chlorides of types $XC_6H_4CH_2Cl$ (X = H, Me and Cl) and $ClCH_2C_6H_4CH_2Cl$ (*o*-, *m*- and *p*-isomers) with methylchlorodisilanes $ClMe_2SiSiMe_2Cl$, $ClMe_2SiSiMeCl_2$ and $Cl_2MeSiSiMeCl_2$ in the presence of $Pd(PPh_3)_4$ to give the corresponding benzylmethylchlorosilanes in good to high yields.

Introduction

The palladium- or nickel-catalyzed Si–Si cleavage reaction of disilanes with organic halides such as allyl chloride and chlorobenzene, formally a dehalogenative silylation (eq. 1), was first reported in the patent literature by Atwell and Bokerman [1]. This reaction is of great importance, since it constitutes a silicon–carbon bond-forming process of a new type and, in fact, considerable effort has been devoted to developing the range of the reaction [2–5].

$$>\!\mathrm{Si{-}Si}\!< + >\!\mathrm{C{-}X} \rightarrow\ >\!\mathrm{Si{-}C}\!< + >\!\mathrm{Si{-}X} \qquad (1)$$

$$(\mathrm{X = Br, Cl, I})$$

Recently, Eaborn and coworkers [3a,c] extended this approach to the successful preparation of p-$O_2NC_6H_4CH_2SiMe_3$ and p-$NCC_6H_4CH_2SiMe_3$ from the corresponding benzyl halides using $Pd(PAr_3)_4$ (Ar = Ph, p-$MeOC_6H_4$ and *p*-

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* For part XI see ref. 6.

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$Me_3SiCH_2C_6H_4$, etc.), thus providing a novel route to such compounds. However, in this instance, it was also mentioned that the silylation of benzyl halides not bearing such strongly electron-withdrawing groups (e.g., $PhCH_2Cl$, *m*-$MeC_6H_4CH_2Br$ and *p*-$MeC_6H_4CH_2Br$, etc.) afforded the benzyltrimethylsilanes only in low yields, due to the competitive coupling of the benzyl halides themselves [3a,c].

In a previous communication [6], we reported our preliminary finding that methylchlorodisilanes such as $ClMe_2SiSiMe_2Cl$, $ClMe_2SiSiMeCl_2$ and $Cl_2MeSiSiMeCl_2$ can effectively silylate benzylic chlorides in the presence of a catalytic amount of $Pd(PPh_3)_4$. This paper is intended to summarize our work on this palladium(0)-catalyzed dechlorinative silylation.

Results and discussion

Examples of the dechlorinative silylation of benzyl chlorides, $XC_6H_4CH_2Cl$ (X = H, Me and Cl), with $ClMe_2SiSiMe_2Cl$ are given in Table 1. Generally, the reaction proceeded satisfactorily at 130°C in the presence of 1 mol% of the palladium(0) complex to reach completion in 2–3 h. Although a small amount of $(XC_6H_4CH_2)_2$ was formed in the silylation with exactly one equiv. of the methylchlorodisilane, this coupling reaction was virtually negligible when a 2–3 fold excess of the disilane was used. For instance, treatment of benzyl chloride with 3 equiv. of the disilane at 130°C for 3 h afforded benzyldimethylchlorosilane exclusively, whereas the use of an equimolar mixture of the reactants led to the formation of a 22% yield of dibenzyl as well as a 79% yield of the benzylsilane. Under optimum conditions the dechlorinative silylation afforded essentially a 1 : 1 mixture of the desired benzyldimethylchlorosilanes and dimethyldichlorosilane.

$$XC_6H_4CH_2Cl + ClMe_2SiSiMe_2Cl \xrightarrow{Pd^0} XC_6H_4CH_2SiMe_2Cl + Me_2SiCl_2 \qquad (2)$$

Table 1 also presents the results of the reaction of $ClMe_2SiSiMe_2Cl$ with the *o*-, *m*- and *p*-isomers of α,α'-dichloroxylene. Although rather vigorous conditions were required to achieve the dechlorinative disilylation exclusively, the corresponding bis(dimethylchlorosilyl)xylenes were obtained in good yields when each isomer was allowed to react with excess (6 equiv.) of the methylchlorodisilane at 150°C in the presence of 1 mol% of the catalyst. These bis(dimethylchlorosilyl)xylenes may be

$$o\text{-}, m\text{-}, \text{or } p\text{-}ClCH_2C_6H_4CH_2Cl + 2\ ClMe_2SiSiMe_2Cl \xrightarrow{Pd^0} o\text{-}, m\text{- or } p\text{-}ClMe_2SiCH_2C_6H_4CH_2SiMe_2Cl + 2\ Me_2SiCl_2 \qquad (3)$$

important precursors for the synthesis of thermally stable poly(tetramethylsilxylylenesiloxanes) [7].

Our previous investigations [2] showed that, in the Si–Si cleavage reaction, introduction of a chlorine atom on silicon increases the reactivity of the disilanes, presumably by increasing the electron-accepting properties of the Si–Si bonds. This is also to be the case in the present silylation. Thus, the reaction of benzyl chlorides with the highly chlorinated disilane, $Cl_2MeSiSiMeCl_2$, occurred at a lower tempera-

TABLE 1

REACTIONS OF $ClMe_2SiSiMe_2Cl$ WITH BENZYLIC CHLORIDES IN THE PRESENCE OF $Pd(PPh_3)_4$ [a]

Benzylic chloride	Temp (°C)	Product		Yield (%) [b]
$PhCH_2Cl$	130	$PhCH_2SiMe_2Cl$	(**1**)	97
o-$MeC_6H_4CH_2Cl$	130	o-$MeC_6H_4CH_2SiMe_2Cl$	(**2**)	98
m-$MeC_6H_4CH_2Cl$	130	m-$MeC_6H_4CH_2SiMe_2Cl$	(**3**)	87
p-$MeC_6H_4CH_2Cl$	130	p-$MeC_6H_4CH_2SiMe_2Cl$	(**4**)	98
o-$ClC_6H_4CH_2Cl$	130	o-$ClC_6H_4CH_2SiMe_2Cl$	(**5**)	95
m-$ClC_6H_4CH_2Cl$	130	m-$ClC_6H_4CH_2SiMe_2Cl$	(**6**)	91
p-$ClC_6H_4CH_2Cl$	130	p-$ClC_6H_4CH_2SiMe_2Cl$	(**7**)	96
o-$(ClCH_2)_2C_6H_4$ [c]	150	o-$(ClMe_2SiCH_2)_2C_6H_4$	(**8**)	70
m-$(ClCH_2)_2C_6H_4$ [c]	150	m-$(ClMe_2SiCH_2)_2C_6H_4$	(**9**)	74
p-$(ClCH_2)_2C_6H_4$ [c]	150	p-$(ClMe_2SiCH_2)_2C_6H_4$	(**10**)	72

[a] Reaction conductions: [benzylic chloride]/[$Me_4Si_2Cl_2$]/[Pd^0] = 1/3/0.01; solvent, mesitylene; reaction time, 2–3 h (unless otherwise indicated). [b] Yields based on the benzylic chloride charged (determined by GLC). [c] [Benzylic chloride]/[$Me_4Si_2Cl_2$]/[Pd^0] = 1/6/0.01; reaction time, 3–5 h.

ture (80°C) compared to the corresponding reaction of $ClMe_2SiSiMe_2Cl$ (Table 2).

$$XC_6H_4CH_2Cl + Cl_2MeSiSiMeCl_2 \rightarrow XC_6H_4CH_2SiMeCl_2 + MeSiCl_3 \qquad (4)$$

Further, the reaction of the unsymmetrical disilane, $ClMe_2SiSiMeCl_2$, with $PhCH_2Cl$ and p-$MeC_6H_4CH_2Cl$ produced the benzylmethyldichlorosilanes almost exclusively rather than the other possible products, benzyldimethylchlorosilanes (Table 2). Predominant formation of methyldichlorosilyl derivatives was also encountered in the corresponding silylation of allyl chloride [2c].

Most of the reactions studied are clean and the simplicity of the procedure for conducting the silylation and work-up permitted a preparative-scale experiment to be carried out with considerable success. For example, $PhCH_2SiMe_2Cl$ and p-

TABLE 2

REACTIONS OF $Cl_2MeSiSiMeCl_2$ (A) OR $ClMe_2SiSiMeCl_2$ (B) WITH BENZYL CHLORIDES IN THE PRESENCE OF $Pd(PPh_3)_4$ [a]

Benzyl chloride	Disilane	Product		Yield (%) [b]
$PhCH_2Cl$	A	$PhCH_2SiMeCl_2$	(**11**)	97
$PhCH_2Cl$	B	$PhCH_2SiMeCl_2$		98
		$PhCH_2SiMe_2Cl$		2
m-$MeC_6H_4CH_2Cl$	A	m-$MeC_6H_4CH_2SiMeCl_2$	(**12**)	87
p-$MeC_6H_4CH_2Cl$	A	p-$MeC_6H_4CH_2SiMeCl_2$	(**13**)	92
p-$MeC_6H_4CH_2Cl$	B	p-$MeC_6H_4CH_2SiMeCl_2$		95
		p-$MeC_6H_4CH_2SiMe_2Cl$		2
o-$ClC_6H_4CH_2Cl$	A	o-$ClC_6H_4CH_2SiMeCl_2$	(**14**)	63
m-$ClC_6H_4CH_2Cl$	A	m-$ClC_6H_4CH_2SiMeCl_2$	(**15**)	94
p-$ClC_6H_4CH_2Cl$	A	p-$ClC_6H_4CH_2SiMeCl_2$	(**16**)	96

[a] Reaction conditions: [benzyl chloride]/[disilane]/[Pd^0] = 1/1–2/0.01; 80°C, 2–10 h; solvent, benzene. [b] Yields based on the benzyl chloride charged (determined by GLC).

$MeC_6H_4CH_2SiMe_2Cl$ were obtained in isolated yields of 68 and 69%, respectively, from the reaction of $ClMe_2SiSiMe_2Cl$ with the corresponding benzyl chlorides. It is also noted that the methylchlorodisilanes are readily available in large quantities [8]. Thus, the present silylation is of value as a quick and direct method for preparing benzylmethylchlorosilanes, although several methods involving the Grignard reaction have been employed for the synthesis of these compounds [9].

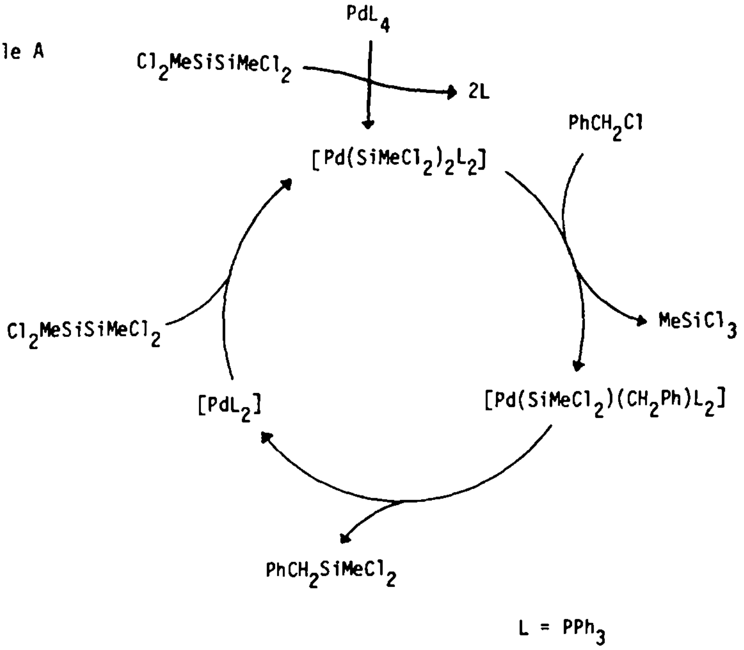
Incidentally, we found that the dechlorinative silylation can be effected at a moderate temperature by using the complex $PdCl(CH_2Ph)(PPh_3)_2$, which is the product of the oxidative addition of benzyl chloride to $Pd(PPh_3)_4$ [10]. For instance, $ClMe_2SiSiMe_2Cl$ reacted with benzyl chloride at 80°C in the presence of 1 mol% of the palladium(II) complex to give $PhCH_2SiMe_2Cl$ in 75% yield after 7 h, whereas no significant reaction occurred in the presence of $Pd(PPh_3)_4$ under comparable conditions. Apparently, the benzylpalladium(II) complex is much more effective than its parent complex. This result is of considerable interest but rather surprising, since benzyl chloride undergoes rapid addition to $Pd(PPh_3)_4$ at room temperature [11]. The very low catalytic activity of the palladium(0) complex in this case might be attributable to deactivation by the triphenylphosphine that the complex liberates [12]. Also, we found that a 1:2 mixture of $PdCl(CH_2Ph)(PPh_3)_2$ and PPh_3 showed no catalytic activity at 80°C for the corresponding silylation, apparently owing to the retardation by the extra ligand.

A competitive experiment to determine relative reactivities of benzyl chlorides toward the silylation was carried out in order to obtain information about the substituent effect on the reaction. In order to do so, two different benzyl chlorides were allowed to react with a limited amount of $Cl_2MeSiSiMeCl_2$ in the presence of the palladium(0) complex at 80°C. The result is as follows; *m*-$MeC_6H_4CH_2Cl$ (1.2), *p*-$MeC_6H_4CH_2Cl$ (2.0), $PhCH_2Cl$ (1.0), *o*-$ClC_6H_4CH_2Cl$ (2.8), *m*-$ClC_6H_4CH_2Cl$ (0.6) and *p*-$ClC_6H_4CH_2Cl$ (1.9). Both *ortho*- and *para*-substituents somewhat accelerate the rate of the reaction. At present, however, we cannot give any consistent explanation to accommodate the observed trend. Presumably, this may reflect a compromise of the controlling factors in the sequence of the steps which are involved in the present catalytic reaction.

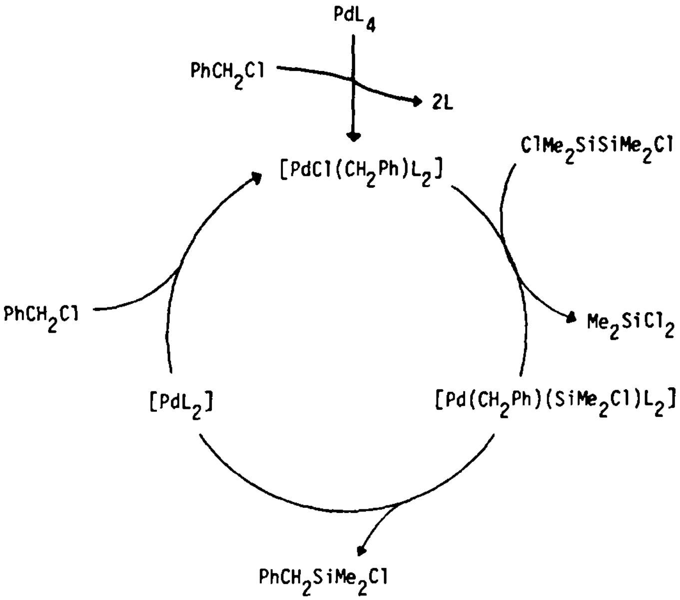
Possible mechanisms for this particular dechlorinative silylation are shown in Scheme 1. Catalytic cycle A was inferred from the recent finding by Eaborn and coworkers [3c] that $Pd(PPh_3)_4$ reacts immediately with $Cl_3SiSiCl_3$ to give the silylpalladium(II) complex $Pd(SiCl_3)_2(PPh_3)_2$ and that this complex can act as a catalyst for the reaction of the perchlorodisilane with some organic halides (e.g., MeBr). The silylation with $Cl_2MeSiSiMeCl_2$ proceeds probably according to this cycle. Actually, we found that the palladium(0) complex reacts with this methylchlorodisilane very rapidly, although an attempt to isolate the expected silylpalladium complex, e.g., $Pd(SiMeCl_2)_2(PPh_3)_2$, failed. Instead, we obtained only $PdCl_2(PPh_3)_2$, even at −78°C. Probably, the bis(methyldichlorosilyl) complex is much less stable compared to the bis(trichlorosilyl) derivative and decomposes to the dichloropalladium(II) complex during the reaction. Cycle B can be envisioned based on the results obtained in the present work; (i) the benzylpalladium(II) complex $PdCl(CH_2Ph)(PPh_3)_2$ is a fairly effective catalyst as described above and (ii) $ClMe_2SiSiMe_2Cl$ did not show a high reactivity toward the palladium(0) complex. Thus, cycle B is likely to be operative for the silylation of benzyl chlorides with $ClMe_2SiSiMe_2Cl$.

SCHEME 1

Cycle A



Cycle B



It is noted that the dichloropalladium(II) complex $PdCl_2(PPh_3)_2$ can also act as a catalyst, but it is rather less effective compared to $Pd(PPh_3)_4$.

Experimental

IR spectra were obtained with a JASCO A102 spectrophotometer. ^1H NMR spectra were taken on a Varian EM-360 spectrometer. GLC analyses were performed on Ohkura 802T and 103 instruments using 0.4 × 100–200 cm Teflon columns packed with 10% Silicone KF-96, 10% DCQF-1 and 15% SE-30 on Celite 545 SK (80–100 mesh). Corrections were made for thermal conductivity of the various components.

Benzyl chlorides and α,α′-dichloroxylenes were commercially available and used without further purification. All solvents were purified and degassed. Disilanes $ClMe_2SiSiMe_2Cl$ [8f], $ClMe_2SiSiMeCl_2$ [8f] and $Cl_2MeSiSiMeCl_2$ [8e] were prepared according to published procedures. Palladium complexes $Pd(PPh_3)_4$ [13], $PdCl_2(PPh_3)_2$ [14] and $PdCl(CH_2Ph)(PPh_3)_2$ [10] were prepared according to literature procedures.

Structural assignments for the benzylmethylchlorosilanes were made, after isolation by GLC separation or distillation, based on their IR and NMR parameters and/or elemental analyses, as shown in Table 3.

TABLE 3

CHARACTERIZATION OF BENZYLMETHYLCHLOROSILANES OBTAINED

Compound	Bp. (°C/mmHg)	NMR (δ, ppm)[a]	Anal. found (calcd.) (%)	
			C	H
1[b]	69/5.0	0.37 (s, 6H), 2.34 (s, 2H), 7.10 (s, 5H)		
2 ($C_{10}H_{15}ClSi$)	84/1.2	0.38 (s, 6H), 2.29 (s, 3H), 2.37 (s, 2H), 6.96 (s, 4H)	60.80 (60.43)	7.69 (7.61)
3 ($C_{10}H_{15}ClSi$)	87/1.2	0.35 (s, 6H), 2.30 (s, 5H), 6.85 (m, 4H)	60.71 (60.43)	7.58 (7.61)
4[b]	87/1.5	0.37 (s, 6H), 2.27 (s, 5H), 6.92 (s, 4H)		
5 ($C_9H_{12}Cl_2Si$)	83/3.5	0.42 (s, 6H), 2.67 (s, 2H), 7.13 (m, 4H)	49.24 (49.32)	5.75 (5.52)
6	94/4.1	0.39 (s, 6H), 2.43 (s, 2H), 7.03 (m, 4H)	49.60 (49.32)	5.62 (5.52)
7[c]	86/3.7	0.38 (s, 6H), 2.29 (s, 2H), 6.89 (d, 2H, $J = 9$ Hz), 7.13 (d, 2H, $J = 9$ Hz)		
8[d]	105/1.0	0.38 (s, 12H), 2.36 (s, 4H), 6.98 (s, 4H)		
9 ($C_{12}H_{20}Cl_2Si_2$)	101/0.4	0.39 (s, 12H), 2.33 (s, 4H), 6.84 (m, 4H)	49.53 (49.47)	6.83 (6.92)
10[e]	—[f]	0.33 (s, 12H), 2.34 (s, 4H), 6.86 (s, 4H)		
11[c]	75/5.0	0.67 (s, 3H), 2.76 (s, 2H), 7.30 (s, 5H)		
12 ($C_9H_{12}Cl_2Si$)	78/2.2	0.67 (s, 3H), 2.32 (s, 3H), 2.57 (s, 2H), 6.98 (m, 4H)	49.55 (49.32)	5.64 (5.52)
13 ($C_9H_{12}Cl_2Si$)	75/0.9	0.68 (s, 3H), 2.32 (s, 3H), 2.58 (s, 2H) 7.02 (m, 4H)	49.45 (49.32)	5.58 (5.52)
14[g]	86/4.0	0.73 (s, 3H), 2.84 (s, 2H), 7.14 (s, 4H)		
15[g]	95/3.0	0.73 (s, 3H), 2.63 (s, 2H), 7.15 (s, 4H)		
16[g]	93/3.0	0.71 (s, 3H), 2.60 (s, 2H), 6.93 (d, 2H, $J = 8$ Hz), 7.17 (d, 2H, $J = 8$ Hz)		

[a] All spectra were taken in CCl_4 using Me_4Si as an internal standard. [b] Ref. 9e. [c] Ref. 9f. [d] This compound gave a poor analytical result due to extremely high susceptibility to hydrolysis. [e] Ref. 9c. [f] Bp. not measured. [g] Ref. 9b.

Procedure for the dechlorinative silylations

The reactions were conducted under nitrogen in a refluxed system. Typical examples are described below.

(a) Reaction of $ClMe_2SiSiMe_2Cl$ with $PhCH_2Cl$. A mixture of 1.27 g (10.0 mmol) of benzyl chloride, 5.62 g (30.0 mmol) of the disilane, 0.12 g (0.10 mmol) of $Pd(PPh_3)_4$ and 5 ml of mesitylene was heated at 130°C (oil bath) with stirring. After 2 h, GLC analysis showed that the reaction had given 9.7 mmol (97% yield based on the benzyl chloride charged) of $PhCH_2SiMe_2Cl$ (**1**). The reaction was also carried out at 130° for 3 h using 1.29 g (10.2 mmol) of benzyl chloride, 1.90 g (10.1 mmol) of the disilane, 0.12 g (0.10 mmol) of the Pd^0 complex and 5 ml of mesitylene. The reaction mixture was found by GLC analysis to contain 8.05 mmol (79% yield) of **1** and 1.15 mmol (22% yield) of $(PhCH_2)_2$. The identity of this coupling product was established by a comparison of its IR spectrum and GLC retention time with those of an authentic sample.

(b) Reaction of $ClMe_2SiSiMe_2Cl$ with p-$ClCH_2C_6H_4CH_2Cl$. A mixture of 1.75 g (10.0 mmol) of the α,α'-dichloroxylene, 11.23 g (60.0 mmol) of the disilane, 0.12 g (0.10 mmol) of the Pd^0 complex and 6 ml of mesitylene was heated at 150°C for 5 h with stirring. GLC analysis disclosed that the dichloroxylene had been completely consumed and that *p*-$ClMe_2SiCH_2C_6H_4CH_2SiMe_2Cl$ (**10**) had been produced in 72% yield.

(c) Reaction of $Cl_2MeSiSiMeCl_2$ with p-$ClC_6H_4CH_2Cl$. A mixture of 1.60 g (9.94 mmol) of the benzyl chloride, 4.58 g (20.1 mmol) of the disilane, 0.12 g (0.10 mmol) of the Pd^0 complex and 5 ml of benzene was heated at 80°C for 6 h with stirring. GLC analysis showed the formation of *p*-$ClC_6H_4SiMeCl_2$ (**16**) in 96% yield.

(d) Reaction of $ClMe_2SiSiMeCl_2$ with $PhCH_2Cl$. A mixture of 1.29 g (10.2 mmol) of benzyl chloride, 3.25 g (20.9 mmol) of the disilane, 0.12 g (0.10 mmol) of the Pd^0 complex and 6 ml of benzene was heated at 80°C for 3 h with stirring. GLC analysis showed that $PhCH_2SiMeCl_2$ (**11**) had been produced in 98% yield together with a 2% yield of **1**.

(e) Reaction of $ClMe_2SiSiMe_2Cl$ with $PhCH_2Cl$ in the presence of $PdCl(CH_2Ph)(PPh_3)_2$. (i) In the absence of the added triphenylphosphine. A mixture of 0.68 g (5.29 mmol) of benzyl chloride, 2.64 g (14.10 mmol) of the disilane, 0.042 g (0.053 mmol) of the Pd^{II} complex, and 4 ml of benzene was heated at 80°C with stirring. After 7 h, GLC analysis showed the formation of **1** in 75% yield. (ii) In the presence of added triphenylphosphine. A mixture of 0.67 g (5.29 mmol) of benzyl chloride, 2.69 g (14.37 mmol) of the disilane, 0.044 g (0.058 mmol) of the Pd^{II} complex, 0.035 g (0.13 mmol) of triphenylphosphine and 4 ml of benzene was heated at 80°C for 7 h with stirring. However, no detectable amount of **1** was formed and the reactants were almost completely recovered.

(f) Reaction of $Cl_2MeSiSiMeCl_2$ with $PhCH_2Cl$ in the presence of $PdCl_2(PPh_3)_2$. A mixture of 1.30 g (10.3 mmol) of benzyl chloride, 4.61 g (20.2 mmol) of the disilane, 0.075 g (0.11 mmol) of the Pd^{II} complex and 3 ml of benzene was heated at 80°C for 10 h with stirring. GLC analysis showed the production of **11** in 39% yield.

Procedure for competitive dechlorinative silylation of benzyl chlorides with $Cl_2MeSiSiMeCl_2$

A typical example is described below. A mixture of 0.630 g (4.98 mmol) of $PhCH_2Cl$, 0.806 g (5.01 mmol) of *p*-$ClC_6H_4CH_2Cl$, 1.09 g (5.84 mmol) of the disilane, 0.057 g (0.051 mmol) of the Pd^0 complex and 4 ml of benzene was heated at 80°C for 3 h. Quantitative analysis by GLC showed that the resulting mixture contained 4.23 mmol of $PhCH_2Cl$ and 3.66 mmol of p-$ClC_6H_4CH_2Cl$. The relative rate was calculated using the following equation [15]:

$$\frac{k(p\text{-}ClC_6H_4CH_2Cl)}{k(PhCH_2Cl)}=\frac{\log[p\text{-}ClC_6H_4CH_2Cl]_i/[p\text{-}ClC_6H_4CH_2Cl]_f}{\log[PhCH_2Cl]_i/[PhCH_2Cl]_f}$$

where $k(p\text{-}ClC_6H_4CH_2Cl)/k(PhCH_2Cl)$ is the ratio of the rate constants for p-$ClC_6H_4CH_2Cl$ and $PhCH_2Cl$, $[p\text{-}ClC_6H_4CH_2Cl]_i$ and $[PhCH_2Cl]_i$ are the initial concentrations of the benzyl chlorides, and $[p\text{-}ClC_6H_4CH_2Cl]_f$ and $[PhCH_2Cl]_f$ are the final concentrations.

Reaction of $Pd(PPh_3)_4$ with $Cl_2MeSiSiMeCl_2$

A mixture of 0.58 g (0.53 mmol) of the Pd^0 complex, 2.50 g (10.9 mmol) of the disilane and 10 ml of benzene was stirred at 20°C for 24 h under nitrogen. The resulting mixture was then diluted with pentane. The yellow microcrystals that separated were filtered, washed with ether and dried in vacuo. IR and far-IR spectra of this product were in complete agreement with those of the complex $PdCl_2(PPh_3)_2$; 0.26 g (75% yield) (Found: C, 61.39; H, 4.45; Cl, 9.66. Calcd. for $C_{36}H_{30}Cl_2P_2Pd$: C, 61.60; H, 4.31; Cl, 10.10%). The reaction was also conducted at temperature of −78°C for 24 h in essentially the same manner as described above. However, only the dichloropalladium(II) complex was obtained from the reaction.

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