Journal of Organometallic Chemistry, 264 (1984) 29–38
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CONVERSION OF DISILANES TO FUNCTIONAL MONOSILANES

XIV *. REACTIONS OF METHYLCHLORODISILANES WITH *gem*-POLYHALIDES CATALYZED BY ORGANIC BASES **

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(Received August 26th, 1983)

Summary

The reaction of methylchlorodisilanes with *gem*-polyhalides in the presence of organic bases has been investigated. The compounds $CXCl_2SiMeCl_2$ (X = Cl, H, F and $SiMeCl_2$) were obtained in moderate to high yields from $Cl_2MeSiSiMeCl_2$ and polyhalomethanes (e.g., CCl_4, $CHCl_3$, $CFCl_3$ and $CCl_3SiMeCl_2$) with PPh_3 or Bu_4NCl as catalyst. The reaction of 1,1,2-trichlorotrimethyldisilane with CCl_4 afforded a 1:1 mixture of $CCl_3SiMeCl_2$ and CCl_3SiMe_2Cl. Also, $XC_6H_4CCl_2$-$SiMeCl_2$ (X = H and 4-Cl) were obtained in moderate yields from $Cl_2MeSiSiMeCl_2$ and $XC_6H_4CCl_3$ with Bu_4NCl or Bu_4NF as catalyst.

Introduction

The metathesis between a disilane and an organic halide (eq. 1) constitutes one of the most important methods for a silicon–carbon bond forming process and

$$\gt Si{-}Si\lt + \gt C{-}X \rightarrow \gt Si{-}C\lt + \gt Si{-}X \qquad (1)$$

considerable effort has been devoted by Atwell and Bokerman [2], us [1,3], Eaborn and coworkers [4] and Yamamoto and coworkers [5] to developing the range of the reaction. It has been thus shown that various organic halides such as allyl, aryl, alkyl, acyl, benzyl and vinyl halides can enter into the metathesis with the aid of palladium(0) and palladium(II) complexes, in combination with a series of methylchlorodisilanes, e.g., $Me_3SiSiMe_3$, $ClMe_2SiSiMe_2Cl$, $Cl_2MeSiSiMe_2Cl$, $Cl_2MeSiSiMeCl_2$ and $Cl_3SiSiCl_3$, etc. Recently, Calas, Dunoguès and coworkers have reported

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* Part XIII see ref. 1.

** This paper is dedicated to Professor Calas on the occasion of his 70th birthday (April 8th, 1984) in recognition of his outstanding researches in Organometallic Chemistry during more than 30 years.

another type of the disilane-mediated silicon–carbon bond forming reaction (eq. 2)

$$RCl + SiCl_4 + Cl_2MeSiSiMeCl_2 \xrightarrow{NiCp_2/HMPA} RSiCl_3 + 2MeSiCl_3 \qquad (2)$$

in which methylchlorodisilanes act as reducing agents rather than silylating agents in a catalytic cycle between $SiCl_4$ and organic halides [6]. In 1971, Benkeser quoted in a review [7] a single example of the base-catalyzed metathesis as illustrated by eq. 3.

$$Cl_3SiSiCl_3 \xrightarrow[\text{0.1 equiv. of } Et_3N]{CCl_4 \text{ (solvent)}} CCl_3SiCl_3(41\%) + SiCl_4 \qquad (3)$$

During the course of a study on the palladium-catalyzed Si–Si cleavage reaction, we found that the reaction between a methylchlorodisilane such as $Cl_2MeSiSiMeCl_2$ and a *gem*-polyhalide such as CCl_4 can also be effected by PPh_3 as catalyst to give (polyhalomethyl)silanes of general formula $CXCl_2SiMe_nCl_{3-n}$ ($X = Cl, H$; $n = 1, 2$) [8]. This paper is intended to summarize our work on the base-catalyzed metathesis and some significant extensions of it.

Results and discussion

The results obtained from the reaction of methylchlorodisilanes with CCl_4 in the presence of organic bases are summarized in Table 1.

Our previous investigations revealed that, in the $Pd(PPh_3)_4$-catalyzed 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 [3,9]. As the table shows, this is also to be the case in the present base-catalyzed silylation. The disilane $Cl_2MeSiSiMeCl_2$ reacted smoothly in the presence of PPh_3 to give essentially a 1 : 1 mixture of (trichloromethyl)methyldichlorosilane (I) and methyltrichlorosilane (eq. 4).

$$Cl_2MeSiSiMeCl_2 + CCl_4 \rightarrow \underset{\text{(I)}}{CCl_3SiMeCl_2} + MeSiCl_3 \qquad (4)$$

The result indicates that reaction 4 is of validity for the synthesis of I which has been

TABLE 1

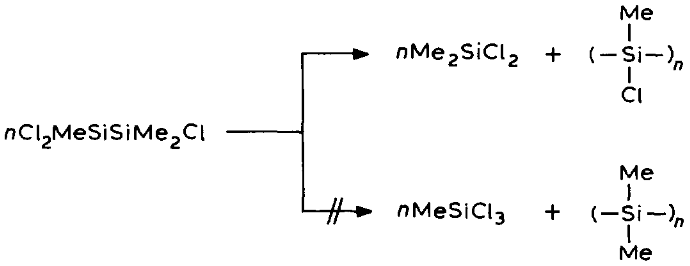
REACTION OF METHYLCHLORODISILANES WITH CARBON TETRACHLORIDE IN THE PRESENCE OF BASIC CATALYSTS [a]

Disilane	Catalyst	Temp. (°C)	Time (h)	Product	Yield [b] (%)
$Cl_2MeSiSiMeCl_2$ [c]	PPh_3	80	2	$CCl_3SiMeCl_2$	100
	Bu_4NCl	80	2		98
	Et_3N	80	6		31
	Bu_3N	80	6		36
$Cl_2MeSiSiMe_2Cl$ [d]	PPh_3	80	1	$CCl_3SiMeCl_2$ (54) [e] CCl_3SiMe_2Cl (46)	95
$ClMe_2SiSiMe_2Cl$	PPh_3	140	15	CCl_3SiMe_2Cl	2
$Me_3SiSiMe_3$	PPh_3	140	20	none	

[a] $[Disilane]/[CCl_4]/[catalyst] = 1/2/0.03$. [b] Yields (based on the disilane charged) were determined by GLC. [c] Similarly, the reaction in the presence of $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $RhCl(PPh_3)_3$, $RuCl_2(PPh_3)_3$ or $NiCl_2(PPh_3)_2$ afforded $CCl_3SiMeCl_2$ in almost quantitative yield (conditions: 80°C, 1–6 h). [d] The reaction in the presence of the Pd^0 catalyst gave a 50/50 mixture of $CCl_3SiMeCl_2$ and CCl_3SiMe_2Cl in 99% combined yield. [e] The ratio was determined by NMR.

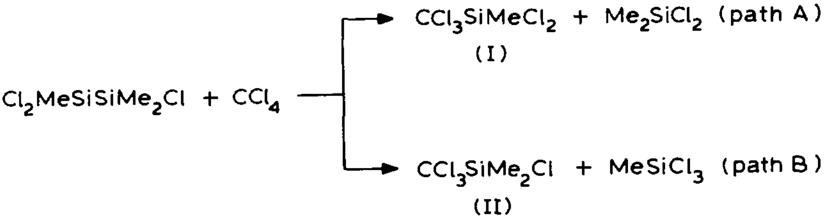
said to be a good dichloromethylene transfer agent [10] and also to serve as precursor of polysilanes of improved flame resistance [11].

It is of interest to see whether or not selective cleavage could occur when the unsymmetrical disilane $Cl_2MeSiSiMe_2Cl$ is employed, since it has been known that this methylchlorodisilane is cleaved by organic bases such as Bu_4PCl, Bu_4NCl and $P(O)(NMe_2)_3$ according to the following scheme [6b, 12].



(5)

As shown in Table 1, both I and (trichloromethyl)dimethylchlorosilane (II) were formed in a ratio of 1/1 when the reaction reached completion. It is, however, noted that a slightly predominance of path A over path B was encountered in the early stage of the reaction and also that the relative amount of I to II decreased with the reaction time. For example, the ratio was 76/24 after 15 min and 61/39 after 40 min. The time-dependent product distribution observed can be explained by assuming that the Si–Si cleavage reaction is followed by the $Si-CCl_3/Si-Cl$ interchange reactions between I and dimethyldichlorosilane and/or II and methyltrichlorosilane (eq. 7).



(6)

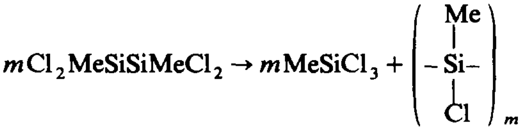
$$\underset{(I)}{CCl_3SiMeCl_2} + Me_2SiCl_2 \rightleftharpoons \underset{(II)}{CCl_3SiMe_2Cl} + MeSiCl_3 \qquad (7)$$

Reactions 4 and 6 were also effected by Group VIII metal complexes such as $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $RuCl_2(PPh_3)_3$, $RhCl(PPh_3)_3$ and $NiCl_2(PPh_3)_2$. However, there were no substantial differences in effectiveness and selectivity between the palladium- and PPh_3-catalyzed reactions. For example, the reaction of the unsymmetrical disilane in the presence of the palladium(0) complex afforded essentially the same result (I/II = 50/50, 99% combined yield) as that of the PPh_3-catalyzed reaction. Thus, it is likely that the catalytic ability of the these complexes is mostly due to the phosphine ligand that these complexes liberate.

We also examined Bu_4NCl, Bu_3N and Et_3N as possible catalysts using the reaction of the tetrachlorodimethyldisilane as model, and found that Bu_4NCl is another satisfactory catalyst. With this catalyst, the reaction proceeded smoothly to afford the silylated product I in almost quantitative yield. The trialkylamines could also induce the reaction, but their catalytic ability was low.

It is further noted that the reaction was very sluggish for $\mathrm{ClMe_2SiSiMe_2Cl}$ and resulted in quite a low yield of the (trichloromethyl)silane II even under forced conditions (Table 1). The low reactivity of the dichlorotetramethyldisilane was also indicated by a competitive experiment in which the disilane was allowed to react with $\mathrm{CCl_4}$ at 100°C in the presence of $\mathrm{PPh_3}$ together with the tetrachlorodimethyldisilane. The dichlorodisilane did not react until most of the tetrachlorodisilane was consumed. The observed trend parallels the reported reactivity order of methylchlorodisilanes toward the base-catalyzed disproportionation [12].

Table 2 shows the results of the reaction of $\mathrm{Cl_2MeSiSiMeCl_2}$ with some other polyhalomethanes. Inspection of the table indicates that the dehalogenative silylation of $\mathrm{CBrCl_3}$ and $\mathrm{CFCl_3}$ proceeds smoothly under mild conditions in the presence of $\mathrm{PPh_3}$ or $\mathrm{Bu_4NCl}$ to afford $\mathrm{CCl_3SiMeCl_2}$ and $\mathrm{CFCl_2SiMeCl_2}$ in high yields. On the other hand, it is also seen from the table that the yields of the expected products are rather low for the less reactive polyhalomethanes $\mathrm{CHCl_3}$ and $\mathrm{CCl_3SiMeCl_2}$, although they can enter into the metathesis under vigorous conditions. The observed low yields are likely to be due to the concurrent occurrence of disproportionation involving Si–Si cleavage (eq. 8). However, the counter product, methyltrichlorosilane, was produced in almost quantitative yield during the reaction, from which much polysilanes were detected. The occurrence of the disproportionation is not unexpected, since several reports have shown that the tetrachlorodimethyldisilane undergoes reaction 8 in the presence of organic bases, e.g., $\mathrm{Bu_4PCl}$, $\mathrm{Bu_4NCl}$, $\mathrm{Me_3N}$ and $\mathrm{P(O)(NMe_2)_3}$ [6b,12].



$$m\mathrm{Cl_2MeSiSiMeCl_2} \rightarrow m\mathrm{MeSiCl_3} + \left(\begin{array}{c} \mathrm{Me} \\ | \\ -\mathrm{Si}- \\ | \\ \mathrm{Cl} \end{array} \right)_m \qquad (8)$$

In an attempt to extend the scope of the present recipe, the interaction of the tetrachlorodimethyldisilane with benzylidyne trichlorides was also examined. It is noted that the reaction of benzylidyne trichlorides with methylchlorodisilanes (e.g., $\mathrm{Me_3SiSiMe_3}$, $\mathrm{ClMe_2SiSiMe_2Cl}$ and $\mathrm{Cl_2MeSiSiMeCl_2}$) in the presence of $\mathrm{Pd(PPh_3)_4}$

TABLE 2

REACTION OF $\mathrm{Cl_2MeSiSiMeCl_2}$ WITH SOME OTHER POLYHALOMETHANES IN THE PRESENCE OF BASIC CATALYSTS [a]

Polyhalomethane	Catalyst	Temp. (°C)	Time (h)	Product	Yield [b] (%)
$\mathrm{CBrCl_3}$	$\mathrm{PPh_3}$	80	2	$\mathrm{CCl_3SiMeCl_2}$	91
$\mathrm{CFCl_3}$	$\mathrm{PPh_3}$	110	5	$\mathrm{CFCl_2SiMeCl_2}$	45
	$\mathrm{Bu_4NCl}$	90	5		94
$\mathrm{CHCl_3}$ [c]	$\mathrm{PPh_3}$	140	4	$\mathrm{CHCl_2SiMeCl_2}$	35
	$\mathrm{Bu_4NCl}$	100	28		27
$\mathrm{CCl_3SiMeCl_2}$	$\mathrm{PPh_3}$	130	15	$\mathrm{CCl_2(SiMeCl_2)_2}$	35
$\mathrm{CH_2Cl_2}$	$\mathrm{Bu_4NCl}$	140	15	none	

[a] [Disilane]/[polyhalomethane]/[catalyst] = 1/2/0.03–0.05. [b] Yields (via GLC) based on the disilane charged. [c] [Disilane]/[$\mathrm{CHCl_3}$] = 1/3.

afforded the coupling products of the chlorides, ArCCl=CClAr (eq. 9), instead of the

$$2ArCCl_3 + 2Cl_2MeSiSiMeCl_2 \rightarrow ArCCl{=}CClAr + 4MeSiCl_3 \tag{9}$$

$$ArCCl_3 + Cl_2MeSiSiMeCl_2 \rightarrow ArCCl_2SiMeCl_2 + MeSiCl_3 \tag{10}$$

silylated products, e.g., $ArCCl_2SiMeCl_2$ [1]. We thus tested PPh_3, Bu_4NCl, Bu_4NF and Bu_3N as possible catalysts to induce either reaction 9 or 10 and found that the ammonium halides are the preferred catalysts for the latter reaction. In the presence of these bases, the tetrachlorodimethyldisilane reacted with $C_6H_5CCl_3$ and $4\text{-}ClC_6H_4CCl_3$ under mild conditions, giving the corresponding (α,α-dichlorobenzyl)methyldichlorosilane. The yields, however, were rather moderate due to the competing disproportionation of the disilane. The results are presented in Table 3.

Although the mechanism of the present silylation has not yet been fully clarified, the following features can be noted.

(1) There is the similarity in the sequence of reactivity for the methylchlorodisilanes in the present silylation and in the base-catalyzed disproportionation as described above, and intermediacy of a silyl anion was proposed for the disproportionation and cleavage reactions of hexachlorodisilane [7,13]. Further, it has been recently reported that the silyl anion Me_3Si^- can be readily generated by the interaction between $Me_3SiSiMe_3$ and Bu_4NF in HMPA [14].

(2) Although most of the reactions listed in Tables 1–3 were carried out without any added solvents, we found that some of the reaction proceeded more smoothly in a polar solvent such as acetonitrile. For example, the reaction of $Cl_2MeSiSiMeCl_2$ with CCl_4 at 80°C in the presence of PPh_3 reached completion after 0.6 h while the corresponding reaction in the absence of this solvent required 2 h of heating. Such a solvent was reported to be essential for the reaction of trichlorosilyl anion generated by the interaction between $HSiCl_3$ and R_3N [7].

(3) In the competitive silylation of benzylidyne trichlorides with $Cl_2MeSiSiMeCl_2$, it was found that an electron-withdrawing substituent (4-Cl) situated on the phenyl ring increased the rate of the reaction ($k_{4\text{-Cl}}/k_H = 1.9$ at 80°C).

(4) A free-radical initiator such as benzoyl peroxide did not induce the silylation to any appreciable extent. The result rules out the possibility of homolytic mechanisms involving S_H2 attack at the Si–Si bonds by a CCl_3 radical.

Further, as regards the catalytic cycle for the reaction induced by PPh_3, it is likely

TABLE 3

REACTION OF $Cl_2MeSiSiMeCl_2$ WITH BENZYLIDYNE TRICHLORIDES IN THE PRESENCE OF BASIC CATALYSTS [a]

Chloride	Catalyst	Product	Yield [b] (%)	Conversion [c] (%)
$C_6H_5CCl_3$	Bu_4NCl	$C_6H_5CCl_2SiMeCl_2$	69	46
	Bu_4NF		71	49
	PPh_3		–	1
	Bu_3N		–	1
$4\text{-}ClC_6H_4CCl_3$	Bu_4NCl	$4\text{-}ClC_6H_4CCl_2SiMeCl_2$	92	52
	Bu_4NF		78	79

[a] $[ArCCl_3]/[disilane]/[catalyst] = 1/1/0.01$; 80°C for 1–4 h. [b] Yields (via GLC) based on the $ArCCl_3$ consumed. [c] Conversion = (mol of $ArCCl_3$ consumed)/(mol of $ArCCl_3$ charged).

that the cycle is initiated by the interaction of PPh_3 with CCl_4 to form the phosphonium chloride $[Ph_3PCCl_3]^+ Cl^-$, since it is known that such a reaction occurs very readily [15]. Thus, a plausible catalytic cycle is illustrated by eqs. 11–13.

$$PPh_3 + CCl_4 \rightarrow \underset{\text{(III)}}{[Ph_3PCCl_3]^+ Cl^-} \qquad (11)$$

$$\text{III} + Cl_2MeSiSiMeCl_2 \rightarrow \underset{\text{(IV)}}{[Ph_3PCCl_3]^+ SiMeCl_2^-} + MeSiCl_3 \qquad (12)$$

$$\text{IV} + CCl_4 \rightarrow \underset{\text{(II)}}{CCl_3SiMeCl_2} + \text{III} \qquad (13)$$

In this cycle, the third step is inferred from the previous finding by Benkeser and coworkers [7] that trichlorosilyl anion is intercepted by CCl_4.

In short, the ready availability of the methylchlorodisilanes [16] and simplicity of the reaction procedure make this approach attractive for the quick and direct synthesis of (polyhalomethyl)silanes. The limitation lies in the fact that $ClMe_2SiSiMe_2Cl$ as well as $Me_3SiSiMe_3$ are virtually unreactive. However, we found that (polyhalomethyl)silanes of types $CXCl_2SiMe_2Cl$ and $CXCl_2SiMe_3$ ($X = Cl$ or F) can be produced via the Si–$CXCl_2$/Si–Cl interchange reaction between $CXCl_2SiMeCl_2$ and Me_2SiCl_2 or Me_3SiCl (eqs. 14 and 15) [13,17].

$$CXCl_2SiMeCl_2 + Me_2SiCl_2 \rightleftharpoons MeSiCl_3 + CXCl_2SiMe_2Cl \qquad (14)$$

$$CXCl_2SiMeCl_2 + Me_3SiCl \rightleftharpoons MeSiCl_3 + CXCl_2SiMe_3 \qquad (15)$$

The Si–Si exchange reaction was found to be effectively promoted also by PPh_3 or Bu_4NCl and the use of the large excess (10 equiv.) of Me_2SiCl_2 or Me_2SiCl_2 to shift the equilibriums almost completely toward the product of the dimethylchloro- and

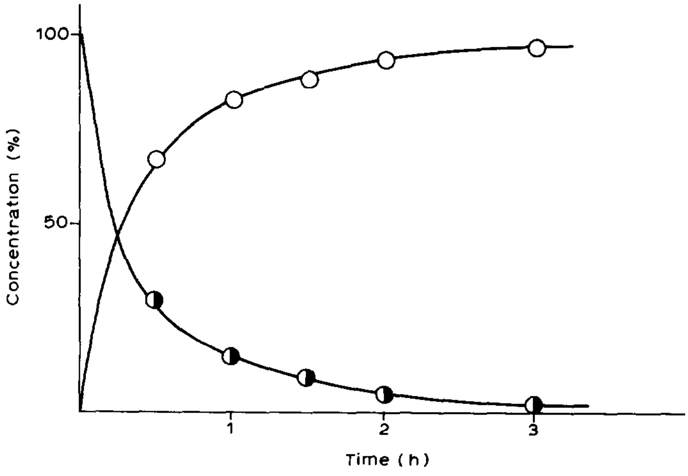


Fig. 1. Typical time-concentration curves for the reaction of $CCl_3SiMeCl_2$ with Me_3SiCl in the presence of Bu_4NCl at 80°C: (○) CCl_3SiMe_3 formation curve; (◑) $CCl_3SiMeCl_2$ disappearance curve.

the trimethyl-derivatives (Fig. 1). Thus, we can readily obtain $CXCl_2SiMe_2Cl$ and $CXCl_2SiMe_3$, when required, in good yield, as illustrated by reactions 16–18.

$$CCl_3SiMeCl_2 \xrightarrow[80^\circ C,\ 1\ h]{Me_2SiCl_2/PPh_3} \underset{(95\%)}{CCl_3SiMe_2Cl} \tag{16}$$

$$CCl_3SiMeCl_2 \xrightarrow[80^\circ C,\ 4\ h]{Me_3SiCl/Bu_4NCl} \underset{(96\%)}{CCl_3SiMe_3} \tag{17}$$

$$CFCl_2SiMeCl_2 \xrightarrow[80^\circ C,\ 1\ h]{Me_3SiCl/Bu_4NCl} \underset{(89\%)}{CFCl_2SiMe_3} \tag{18}$$

Experimental

Boiling and melting points were uncorrected. IR spectra were recorded on a JASCO-102A spectrometer. ^1H NMR spectra were taken on a Varian EM-360 spectrometer using Me_4Si as internal standard. Mass spectra were obtained with JEOL JMS-7 spectrometer. GLC analyses and separations were performed on an Ohkura 102T instrument with thermal conductivity detector using Teflon and Pyrex glass columns (0.4 x 100–200 cm) packed with 10% SE-30, 10% KF-96 and 15% DCQF-1 on Celite 545 (80/100 mesh). GLC yields were calculated by using internal standards after determination of the appropriate response factors.

Organic bases and reagents were commercially available and used as received. The chlorodisilanes $Cl_2MeSiSiMeCl_2$ [16a], $Cl_2MeSiSiMe_2Cl$ [16b] and $ClMe_2SiSiMe_2Cl$ [16b] were prepared according to published procedures. Hexamethyldisilane was commercially available and used as received. The complexes $Pd(PPh_3)_4$ [18], $PdCl_2(PPh_3)_2$ [19], $RuCl_2(PPh_3)_3$ [20], $RhCl(PPh_3)_3$ [21] and $NiCl_2(PPh_3)_2$ [22] were prepared according to literature directions.

Procedure for the reactions of methylchlorodisilanes with gem-polyhalides

The reactions were conducted under nitrogen either in a refluxed system or in a sealed stainless steel reaction vessel. Typical examples are described below.

Reaction of $Cl_2MeSiSiMeCl_2$ with CCl_4 in the presence of PPh_3. A solution of 16.0 g (70 mmol) of the disilane, 21.5 g (140 mmol) of the chloride and 0.55 g (2.1 mmol) of the phosphine was heated at 80°C for 2 h with stirring. GLC analysis showed that the disilane had been completely consumed and that $CCl_3SiMeCl_2$ (I) had been produced in quantitative yield (based on the disilane charged) together with $MeSiCl_3$. Evaporation of the low-boiling materials and subsequent sublimation of the residue afforded 10.1 g (62% yield) of I as colorless cystals.

The reaction was also carried out in acetonitrile (6 ml) at 80°C using 3.42 g (15 mmol) of the disilane, 4.62 g (30 mmol) of the chloride and 0.12 g (0.45 mmol) of the phosphine. After 0.6 h, GLC analysis showed that the disilane had been completely consumed and that I had been produced in 98% yield.

Reaction of $Cl_2MeSiSiMe_2Cl$ with CCl_4 in the presence of PPh_3. A solution of 3.11 g (15 mmol) of the disilane, 4.62 g (30 mmol) of the chloride and 0.12 g (0.45 mmol) of the phosphine was heated at 80°C for 1 h with stirring. GLC and NMR analyses showed that the reaction had given a 54/46 mixture of I and CCl_3SiMe_2Cl (II) in 95% combined yield.

Reaction of $ClMe_2SiSiMe_2Cl$ with CCl_4 in the presence of PPh_3. A solution of 1.88 g (10 mmol) of the disilane, 3.08 g (20 mmol) of the chloride and 0.08 g (0.3 mmol) of the phosphine was heated at 140°C for 15 h in a 50 ml sealed stainless steel reaction vessel. GLC analysis showed that II had been produced in 2% yield with the consumption of 5% of the disilane.

Reaction of $Cl_2MeSiSiMeCl_2$ with CCl_4 in the presence of $Pd(PPh_3)_4$. A solution of 3.47 g (15 mmol) of the disilane, 4.62 g (30 mmol) of the chloride, 0.12 g (0.45 mmol) of the complex and 5 ml of toluene was heated at 80°C with stirring. After 1 h, GLC analysis showed the production of I in 98% yield.

Reaction of $Cl_2MeSiSiMeCl_2$ with $CFCl_3$ in the presence of Bu_4NCl. A 200 ml stainless steel reaction vessel was charged with 22.9 g (100 mmol) of the disilane, 28.0 g (210 mmol) of the halide and 0.22 g (0.78 mmol) of the ammonium chloride. The vessel was sealed and heated at 90°C for 5 h. GLC analysis showed the formation of $CFCl_2SiMeCl_2$ in 94% yield. Work-up gave 7.6 g (34% yield) of the product as colorless crystals.

Reaction of $Cl_2MeSiSiMeCl_2$ with $CHCl_3$ in the presence of PPh_3. A solution of 22.8 g (100 mmol) of the disilane, 35.8 g (300 mmol) of the chloride and 0.79 g (3 mmol) of the phosphine was heated at 140°C for 4 h in a 200 ml sealed stainless steel reaction vessel. GLC analysis disclosed that the disilane had been completely consumed and that $CHCl_2SiMeCl_2$ had been produced in 35% yield together with $MeSiCl_3$ (98%) and polysilanes whose structures had not been determined. Work-up gave 5.7 g (29% yield) of the (dichloromethyl)silane as a colorless liquid.

Reaction of $Cl_2MeSiSiMeCl_2$ with $C_6H_5CCl_3$ in the presence of Bu_4NCl. A solution of 2.28 g (10 mmol) of the disilane, 1.95 g (10 mmol) of the chloride and 0.029 g (0.1 mmol) of the ammonium chloride was heated at 80°C for 2 h with stirring. GLC analysis of the resulting mixture disclosed that 46% of benzylidyne trichloride had reacted to produce $C_6H_5CCl_2SiMeCl_2$ in 69% yield (based on the chloride consumed), while the disilane had been completely consumed.

Reaction of $Cl_2MeSiSiMeCl_2$ with 4-$ClC_6H_4CCl_3$ in the presence of Bu_4NCl. A solution of 1.15 g (5 mmol) of the disilane, 1.16 g (5 mmol) of the chloride, 0.02 g (0.05 mmol) of the ammonium chloride and 2 ml of toluene was heated at 80°C for 1 h with stirring. GLC analysis showed the formation of 4-$ClC_6H_4CCl_2SiMeCl_2$ in 92% yield with 52% conversion.

Structural assignments for the products obtained were made based on their IR, ^1H NMR and mass spectra and/or elemental analyses.

These data are given below. I: m.p. 101°C (lit. 23 m.p. 99°C); ^1H NMR (CCl_4) δ 1.11 ppm (s); IR (KBr disk) 1260 and 700–800 cm^{-1}.

II: m.p. 119–120°C (lit. 17 m.p. 122°C); ^1H NMR (CCl_4) δ 0.75 ppm (s); IR (KBr disk) 1255 and 700–800 cm^{-1}.

$CHCl_2SiMeCl_2$ [24]: b.p. 55–58°C (50 mmHg); ^1H NMR (CCl_4) δ 1.00 (s, 3H) and 5.39 ppm (s); IR (neat) 1255 and 710–800 cm^{-1}.

$CFCl_2SiMeCl_2$: ^1H NMR (CCl_4) δ 1.08 ppm (s); IR (KBr disk) 1260 and 700–800 cm^{-1}; Mass (20 eV) m/e 187 (M^+); Anal. Found: C, 13.52; H, 1.73. $C_2H_3Cl_4FSi$ calcd.: C, 12.79; H, 1.61%.

$CCl_2(SiMeCl_2)_2$: ^1H NMR (CCl_4) δ 1.15 ppm (s); IR (KBr disk) 1255 and 700–800 cm^{-1}; Mass (20 eV) m/e 310 (M^+); Anal. Found: C, 11.17; H, 2.00. $C_3H_6Cl_6Si_2$ calcd.: C, 11.59; H, 1.94%.

$C_6H_5CCl_2SiMeCl_2$: ^1H NMR (CCl_4) δ 1.00 (s, 3H), 7.37 (m, 3H) and 7.70 ppm (m, 2H); IR (neat) 1260 cm^{-1}; Mass (20 eV) *m/e* 272 (M^+); this compound gave a poor analytical result due to high susceptibility to hydrolysis. 4-$ClC_6H_4CCl_2SiMeCl_2$: ^1H NMR (CCl_4) δ 1.08 (s, 3H), 7.35 (d, 2H, *J* 8 Hz) and 7.65 ppm (d, 2H, *J* 8 Hz); IR (neat) 1260 cm^{-1}; Mass (20 eV) *m/e* 303 (M^+); this compound also gave a poor analytical result due to high susceptibility to hydrolysis.

Procedure for the competitive reactions

Competitive reaction of chlorodisilanes with CCl_4 in the presence of PPh_3. A solution of 1.14 g (5 mmol) of $Cl_2MeSiSiMeCl_2$, 0.94 g (5 mmol) of $ClMe_2SiSiMe_2Cl$, 3.08 g (20 mmol) of the chloride and 0.079 g (0.3 mmol) of the phosphine was heated at 100°C for 1.5 h with stirring. GLC and NMR analyses showed that 4.8 mmol of the tetrachlorodimethyldisilane had reacted to produce 4.6 mmol of I, whereas the dichlorotetramethyldisilane had remained intact and no trace of II had been produced.

Competitive reaction of benzylidyne trichlorides with $Cl_2MeSiSiMeCl_2$ in the presence of Bu_4NF. A solution of 1.95 g (10 mmol) of $C_6H_5CCl_3$, 2.32 g (10 mmol) of 4-$ClC_6H_4CCl_3$, 1.14 g (5 mmol) of the disilane, 0.1 mL of a tetrahydrofuran solution of the ammonium fluoride (1 mol solution, 0.1 mmol) and 2 ml of toluene was heated at 80°C for 1 h. GLC analysis showed the formation of 0.76 mmol of $PhCCl_2SiMeCl_2$ and 1.42 mmol of 4-$ClC_6H_4CCl_2SiMeCl_2$. The relative rate (k_{rel}) of 1.9 was obtained using the following equation [25]:

$$k_{rel} = \frac{k_{4\text{-}Cl}}{k_H} = \frac{[C_6H_5CCl_3]_i}{[4\text{-}ClC_6H_4CCl_3]_i} \times \frac{[4\text{-}ClC_6H_4CCl_2SiMeCl_2]_f}{[C_6H_5CCl_2SiMeCl_2]_f}$$

where $k_{4\text{-}Cl}/k_H$ is the ratio of the rate constants for 4-$ClC_6H_4CCl_3$ and $C_6H_5CCl_3$, $[4\text{-}ClC_6H_4CCl_3]_i$ and $[C_6H_5CCl_3]_i$ are the initial concentrations of the benzylidyne trichlorides and $[4\text{-}ClC_6H_4CCl_2SiMeCl_2]_f$ and $[C_6H_5CCl_2SiMeCl_2]_f$ are molar amounts of the (α,α-dichlorobenzyl)methyldichlorosilanes produced.

Procedure for the Si–$CXCl_2$/Si–Cl interchange reactions

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

Reaction of $CFCl_2SiMeCl_2$ with Me_3SiCl in the presence of Bu_4NCl. A solution of 2.16 g (10 mmol) of $CFCl_2SiMeCl_2$, 10.9 g (100 mmol) of Me_3SiCl and 0.083 g (0.30 mmol) of the ammonium chloride was heated at 80°C with stirring. After 1 h, GLC analysis disclosed that $CFCl_2SiMeCl_2$ had virtually disappeared and that $CFCl_2SiMe_3$ had been produced in 89% yield.

Time-concentration curves for the reaction of $CCl_3SiMeCl_2$ with Me_3SiCl in the presence of Bu_4NCl. A solution of 1.16 g (5 mmol) of $CCl_3SiMeCl_2$, 5.43 g (50 mmol) of Me_3SiCl, 0.042 g (0.15 mmol) of the ammonium chloride and 0.722 g (5 mmol) of n-decane as internal standard was heated at 80°C with stirring and the course of the reaction was monitored by GLC. The results are shown in Fig. 1.

CCl_3SiMe_3: m.p. 128–129°C (lit. 26 m.p. 130°C); ^1H NMR (CCl_4) δ 0.32 ppm (s); IR (KBr disk) 1255 cm^{-1}. $CFCl_2SiMe_3$: ^1H NMR (CCl_4) δ 0.31 ppm (s); IR (neat); 1256 cm^{-1}; Anal. Found: C, 24.04; H, 4.73. $C_4H_9Cl_2FSi$ calcd.: C, 23.63; H, 5.18%.

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