570 *Organometallics* **1998,** *17,* 570−573

Palladium-Catalyzed Selective Dechlorination of Polychloromethylsilanes with Trichlorosilane

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Received June 10, 1997

Selective dechlorination of the chloromethyl-containing silanes $(Cl_{3-n}CH_n)SiCl_{3-m}Me_m$ ($n = 0-2$ (**1**−**3**), $m = 0-3$ (**a**−**d**)) with trichlorosilane was studied in the presence of group 10 transition-metal compounds at reaction temperatures between 100 and 150 °C in sealed bombs. The reactions give the corresponding less chlorinated compounds in good yields without reducing Si−Cl bonds, only when $Pd(OAc)_2$ and $PdCl_2$ were used as catalysts. The dechlorination rate of chlorinated methylchlorosilanes depends on the substituents on silicon and the number of chlorine atoms on the chlorinated carbon: the rate increases as the number of chlorine atoms on carbon and of methyl groups on silicon increase. The reactivity difference between (trichloromethyl)-, (dichloromethyl)-, and (monochloromethyl)chlorosilanes allows selective stepwise reduction from $SiCCl_3$ to $SiCHCl_2$ to $SiCH_2Cl$ and, finally, to $SiCH_3$ by controlling the amount of trichlorosilane reductant and the reaction conditions. The catalytic reactivity of transition-metal compounds decreases in the following order: $Pd(OAc)_2 > PdCl_2 >> Pt-C$, H_2PtCl_6, $Ni(OAc)_2$, $NiCl_2 > Pd(PPh_3)_2Cl_2$, K_2PtCl_4.

Introduction

The reductive dehalogenation of organic halides in the field of organic synthesis has been well-defined, and numerous reducing agents have been reported in many articles and reviews.[1,2] Among various reducing reagents and procedures developed for the simple, economical, selective dechlorination of organic halides, Si−H bond containing trialkylsilanes[3] such as triethylsilane, tributylsilane, and butylsilane have been known to be effective reducing agents. Transition-metal compounds such as palladium metal on charcoal, organotin hydrides, and palladium chloride have been reported to catalyze the reduction of organic chlorides with trialkylsilanes.[3]

Although Bürger and Moritz in 1992 first reported the reduction of (fluorochloromethyl)trichlorosilanes with lithium aluminum hydride or organotin hydrides, the reduction gave all dechlorinated methylsilane products with no selectivity.[4] The selective dechlorination of C−Cl bonds of chlorinated alkyl group containing organochlorosilanes, known as useful starting materials for fungicides in industry,[5] without reduction of Si−Cl bonds has attracted little attention and has remained unexploited due to the lack of proper reducing agents.

(Chloromethyl)methyldichlorosilane has been prepared by the photochlorination[6] of dimethyldichlorosilane on a large scale. In this process, polychlorinated methylsilanes such as (dichloromethyl)methyldichlorosilane and (trichloromethyl)methyldichlorosilane are inevitably produced as byproducts, because chlorinated organic moieties are more susceptible toward the chlorination.[6] Thus, it is very important to develop methods for a selective reduction of polychlorinated byproducts to useful, less chlorinated compounds. We wish to report a selective reduction of (polychloromethyl)chlorosilanes with readily available trichlorosilane in the presence of group 10 transition-metal compounds.

Results and Discussion

Dechlorination of (Polychloromethyl)chlorosilanes with Trichlorosilane. The reductive dechlorination of (trichloromethyl)trichlorosilane (**1a**) with 5 molar equiv of trichlorosilane in the presence of pal-

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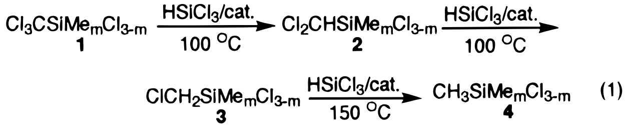
S0276-7333(97)00490-1 CCC: $15.00

Table 1. Results on Dechlorination[a] of (Polychloromethyl)silanes ($Cl_nCH_{3-n}SiMe_mCl_{3-m}$)

entry no.	reactant (n; m)	conditions temp (°C)	time (h)	product yields[b] (%) major (n; m)		minor	
1	**1a** (3; 0)	100	6.0	**2a**	76	**3a**	14
2	**1b** (3; 1)	100	4.0	**2b**	82	**3b**	13
3	**2a** (2; 0)	100	10.5	**3a**	67	**4a**	15
4	**2b** (2; 1)	100	8.5	**3b**	70	**4b**	16
5	**2c** (2; 2)	100	7.0	**3c**	73	**4c**	14
6	**2d** (2; 3)	100	7.0	**3d**	77	**4d**	16
7	**3a** (1; 0)	150	12.0	**4a** (0; 0)	70		
8	**3b** (1; 1)	150	12.0	**4b** (0; 1)	73		
9	**3c** (1; 2)	150	12.0	**4c** (0; 2)	80		
10	**3d** (1; 3)	150	12.0	**4d** (0; 3)	91		

[a] Mole ratio of chlorinated methylsilanes to $HSiCl_3$ to $Pd(OAc)_2$ 1:5:0.001. [b] GLC yields.

ladium diacetate as catalyst at 100 °C for 6 h gave (dichloromethyl)trichlorosilane (**2a**) as the major product in 76% yield and the double-reduction product (chloromethyl)trichlorosilane (**3a**) as a byproduct in 14% yield. The reduction of (trichloromethyl)methyldichlorosilane (**1b**) proceeded at a slightly faster rate than that of **1a** and gave (dichloromethyl)methyldichlorosilane (**2b**; 82%) and (chloromethyl)methyldichlorosilane (**3b**; 13%), demonstrating the higher reactivity of **1b** *vs* **1a**. From the reduction of $Cl_2HCSi(CH_3)_mCl_{3-m}$ compounds (**2a**−**d**), faster reduction rates and slightly higher yields were observed for higher methyl substituted silyl compounds. The reduction of monochloromethyl group containing silanes (**3a**−**d**) to the corresponding methylsilanes (**4a**−**d**) required a higher reaction temperature (150 °C) and longer time (12 h) to give yields comparable to those obtained with di- and trichloromethyl group containing silanes. The results show that the Si−H/C−Cl exchange reactions between trichlrosilane and chloromethyl group containing silanes occur stepwise (eq 1). The results are summarized in Table 1.



As shown in Table 1, the reduction of various chloromethylsilanes with trichlorosilane under controlled conditions gave the corresponding one less chlorinated methylchlorosilane products in good conversion (67−91%) yields. The dechlorination rate of (polychloromethyl)silanes varies depending upon the number of chlorine substituents on carbon and the electron-donating nature of the substituents on silicon. The reduction rate increases smoothly as the number of chlorines on the chlorinated carbon increases and increases drastically as the number of methyl groups on silicon increases. It is known that the inductive effects[7,8] of substituents on the chlorinated carbon as well as on the silicon atom play an important role in the catalytic dechlorination using palladium compounds.

Table 2. Catalytic Activities of Group 10 Transition-Metal Compounds for Reduction of $ClCH_2SiMeCl_2$ (3b) to Me_2SiCl_2 (4b)[a]

catalyst	yield of **4b** (%)[b]	catalyst	yield of **4b** (%)[b]
$Pd(OAc)_2$	66	$PtCl_2(PPh_3)_2$	trace[c]
$PdCl_2$	56	K_2PtCl_4	
$PdCl_2(PPh_3)_2$	c	H_2PtCl_6	trace
$Ni(OAc)_2$	trace	Pt/C	trace
$NiCl_2$	trace		

[a] Mole ratio of $ClCH_2SiMeCl_2$ (**3b**) to $HSiCl_3$ to catalyst 1:5: 0.001. [b] GLC yield. [c] The redistribution of trichlorosilane to tetrachlorosilane and dichlorosilane occurred.

On a preparative (0.31 mol) scale, the reaction of (dichloromethyl)methyldichlorosilane (**2b**) with trichlorosilane in the presence of palladium diacetate at 100 °C was carried out in a sealed tube. After 12 h, (chloromethyl)methyldichlorosilane **3b** (60%) was obtained as the major dechlorinated product along with dimethyldichlorosilane (**4b**; 2%) and unreacted **2b** (36%). The reaction of **2b** on a large scale took a longer time and gave a slightly lower yield compared with entry 4 of Table 1, probably due to the inefficient mixing of the reactants in a sealed tube.

Catalytic Activities of Transition-Metal Compounds. Chatgilialoglu *et al.*[9] reported that triethylsilane itself is a poor reducing or an inert agent for the reductive dechlorination of organic halides but that the reducing ability can be improved by adding palladium dichloride. Nickel and platinum compounds also are known to promote the reduction of phenyl halides by triethylsilane.[3c] To look for the best catalyst for the dechlorination of chlorinated methylsilanes with trichlorosilane, **3b** as a representative compound was reduced to **4b** using various group 10 transition-metal compounds at 150 °C for 12 h. The results are summarized in Table 2.

As Table 2 shows, the catalytic activity of transition-metal compounds for the reduction of **3b** to **4b** with trichlorosilane decreases in the order $Pd(OAc)_2 > PdCl_2 >> Pt-C, H_2PtCl_6, Ni(OAc)_2, NiCl_2 > Pd(PPh_3)_2Cl_2, K_2PtCl_4$. Among the group 10 transition-metal compounds tested, palladium compounds show good catalytic activity, while platinum and nickel compounds are not very active. Among palladium compounds, palladium diacetate is more active than palladium dichloride, but $Pd(PPh_3)_2Cl_2$ is not active. It has been reported that fine black particles formed from the trimeric, soluble palladium diacetate[10] in organic solvents are more effective than black particles derived from insoluble polymeric palladium dichloride[11] from the point of view of the reactive surface area of the active species. Although $Pd(PPh_3)_2Cl_2$ is not active for the reduction, it promoted the redistribution of trichlorosilane to tetrachlorosilane and dichlorosilane.

Reducing Ability of Silanes. The effect of substituents on silicon was studied by comparing the dechlorinations of **3b** to **4b** using trichlorosilane and triethylsilane as reductants in the presence of 0.1 mol % palladium diacetate catalyst. The results are listed in Table 3.

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Table 3. Reactivity of Silanes for Reduction of $ClCH_2SiMeCl_2$ (3b) to Me_2SiCl_2 (4b)[a]

	reacn conditions		
silane	temp (°C)	time (h)	**4b** yield (%)[b]
$HSiCl_3$	150	12	66
$HSiEt_3$	150	0.5	83
$HSiEt_3$	107−108[c]	2	65

[a] Mole ratio of **3b** to silane to palladium diacetate 1:5:0.001. [b] GLC yield. [c] Reflux temperature of triethylsilane.

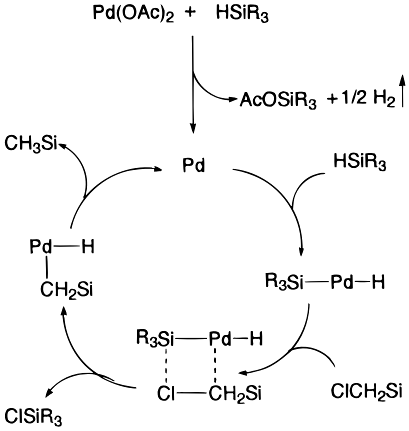
The reduction of **3b** using trichlorosilane at 150 °C for 12 h gave **4b** in 66% yield. However, an 83% yield of **4b** was obtained in a 0.5 h reaction when triethylsilane was used. The conversion yield of **3b** to **4b** with triethylsilane at 107 °C for 2 h in an open system was comparable to the result with trichlorosilane at 150 °C for 12 h. Thus, triethylsilane is a much more active reducing agent than trichlorosilane. This can be rationalized in terms of the electron-donating effect of ethyl groups which enhances the hydridic character of the Si−H bond while the electron-withdrawing effect of chlorine reduces it. Although triethylsilane is a better reducing agent in the present application than trichlorosilane, it is more expensive and the Et_3SiCl formed is more difficult to separate from the products than the lower boiling $SiCl_4$.

Reaction Mechanism. It is well-documented that the reduction of alkyl or aryl halides with triethylsilane in the presence of palladium dichloride as catalyst involves the formation of metallic palladium by reduction of $PdCl_2$ by Et_3SiH.[9] Subsequent oxidative addition of the Si−H bond to the Pd(0) thus generated to give a Si−Pd bonded species, followed by a metathesis reaction between this bond and the alkyl halide, was the reaction course proposed for the synthesis of organohalosilanes in the case of the Si−H/C−I exchange reaction.[12] In order to provide further information concerning the reaction pathway of the palladium diacetate catalyzed dechlorination reaction, palladium diacetate was treated with five equiv of trichlorosilane at room temperature for 30 min. Black palladium powder precipitated, and dihydrogen gas was detected in the off-gases. Acetoxytrichlorosilane was obtained, together with diacetoxydichlorosilane and tetrachlorosilane as disproportionation products, respectively, as shown in eq 2.

$$\begin{aligned} Pd(OAc)_2 + HSiCl_3 \xrightarrow{RT} {} & Pd + H_2 + AcOSiCl_3 + \\ & (AcO)_2SiCl_2 + SiCl_4 + \text{others} \end{aligned} \qquad (2)$$

When the precipitated black palladium powder was washed with hexane[13] and tested for the dechlorination of **2b** under the same conditions, the yield (31%) of **3b** was lower than 70% in entry 4 of Table 1. This black palladium powder showed the catalytic activity in three consecutive runs of the reduction, although the activity decreased slightly as the reduction using the same catalyst was repeated.

Scheme 1



On the basis of the analogy to the deiodination of alkyl iodides with trialkylsilanes,[12] a possible mechanism for the reduction of chloromethyl-containing silanes with trichlorosilane is illustrated in Scheme 1. The black palladium powder is the catalytically active species, generated by the reduction of palladium diacetate with trichlorosilane at the beginning stage of the reaction. It then catalyzes the dechlorination reaction of C−Cl with Si−H in three steps: (1) Si−H oxidative addition to the palladium catalyst to generate a H−Pd−Si species of unknown constitution, (2) metathesis of Pd−Si and C−Cl to give Si−Cl, and (3) C−H reductive elimination from H−Pd−C leading to the dechlorination product. However, our results do not rule out a radical mechanism,[9,14,15] $Pd(H)_x$,[16] or Pd(IV) intermediate.[17]

In conclusion, the dechlorination of polychlorinated methylsilanes with trichlorosilane in the presence of a palladium catalyst gives less chlorinated methylsilanes without reduction of Si−Cl bonds in good yields through stepwise Si−H/C−Cl exchange reactions. This reaction is a practical method for the selective reductions of polychlorinated methylsilanes to useful, less chlorinated chloromethylsilanes.

Experimental Section

Reagents and Physical Measurements. All reactions were carried out in flame-dried glassware or stainless steel bombs. All air-sensitive liquids were transferred by a standard syringe or double-tipped-needle techniques.[18] Silanes, trichlorosilane, (chloromethyl)silanes, (dichloromethyl)silanes, (trichloromethyl)silanes, etc. were purchased from Hüls America Inc. or Aldrich Chemical Co. or prepared by literature procedures.[6] $Pd(OAc)_2$, $PdCl_2$, $Pd(PPh_3)_2Cl_2$, $Ni(OAc)_2$, $NiCl_2$, K_2PtCl_4, and H_2PtCl_6 were purchased from Aldrich Chemical Co. Platinum on charcoal black (Pt, 1%) was purchased from Alfa Products Co. Reaction mixtures were analyzed by GLC on a 1.5 m by $^1/_8$ in. stainless steel column packed with 10% SE-30 or SE-54 on 80−100 mesh Chromosorb P/AW with a Varian 3300 gas chromatograph, thermal conductivity detector, and Varian 4290 integrator. Product yields were determined by GLC

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(13) In response to an editor's suggestion, an attempt to analyze black palladium powders obtained from the reaction of palladium diacetate and palladium dichloride with trichlorosilane was taken. IR spectra for both intractable black powders insoluble in solvents showed no significant bands (particularly $Pd(H)_x$) except for 1632 cm^{-1} ($\nu_{C=O}$) due to a trace of acetoxy group on palladium powder in the former case.

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using *n*-dodecane as the internal standard. Proton and carbon NMR spectra were determined on a Varian Gem 300 spectrometer. Mass spectra were obtained using a Hewlett-Packard 5890 GC/MS. Infrared (IR) spectra were recorded on a Perkin-Elmer 16F PC FT-IR. KBr pellets for the characterization of catalytically active species were made under an atmosphere of argon in a drybox.

General Procedure for the Dechlorination of (Polychloromethyl)silanes. In a 25 mL sealed stainless steel bomb was charged 0.015 mmol of the transition-metal catalyst, 15 mmol of the chlorinated methylchlorosilane, 10.16 g (75 mmol) of trichlorosilane, and 0.5 mL (0.38 g) of dodecane as an internal standard. The reactions were carried out at temperatures of 100 or 150 °C and the progress of the reactions was monitored by GLC at 30 min or 1 h time intervals.

Dechlorination of (Dichloromethyl)methyldichlorosilane (2b) on a Preparative Scale. In a 500 mL sealed stainless steel bomb was charged 70 mg (0.31 mmol) of palladium diacetate, 60.9 g (307.5 mmol) of **2b**, and 210 g (1550 mmol) of trichlorosilane. The reaction was carried out at 100 °C for 12 h. The reaction mixture was transferred to a 500 mL one-necked flask and was separated from palladium catalyst by a bulb-to-bulb vacuum distillation. Distillation at atmospheric pressure gave a mixture (205 g) of trichlorosilane and tetrachlorosilane, **3b** (30.3 g, 60%), and **4b** (0.7 g, 2%). Unreacted **2b** (21.9 g, 36%) also was recovered.

General Procedure for the Dechlorination of 3b with Trichlorosilane Using Various Group 10 Transition-Metal Compounds. In a 25 mL sealed stainless steel bomb was charged 0.015 mmol of the transition-metal compound, 2.45 g (15 mmol) of **3b**, 10.16 g (75 mmol) of trichlorosilane, and 0.5 mL (0.38 g) of dodecane as an internal standard under dry nitrogen at room temperature. The reaction was carried out at 150 °C for 12 h. The conversion yield of **3b** to **4b** was determined by GLC.

Reaction of $Pd(OAc)_2$ with Trichlorosilane. To a stirred solution of palladium diacetate (1.02 g, 4.54 mmol) and dodecane (1 mL, 0.76 g) as an internal standard was added 2.3 mL (22.7 mmol) of trichlorosilane at room temperature under a nitrogen atmosphere over 30 min. Hydrogen gas was detected in the off-gases, and black palladium powder precipitated. The reaction mixture consisted of acetoxytrichlorosilane[19] (16%), pentachlorodisiloxane[20] (9%), diacetoxydichlorosilane[19] (3%), trichlorosilane (20%), tetrachlorosilane (51%), and traces of acetic acid and acetyl chloride by GLC. The products were identified by the analysis of GC/MS spectra and by the comparison with authentic samples obtained from commercial sources. The black palladium powder (0.493g) was obtained by washing three times with hexane solvent (30 mL) and drying and used in part in the next step. The black palladium powder is insoluble in general organic solvents. IR data for black palladium powder (KBr pellet): 1632 cm^{-1} (ν_{CO}).

Black Palladium Powder Catalyzed Dechlorination of 2b by Trichlorosilane. In a 25 mL sealed stainless steel bomb were charged 2.0 mg (about 0.019 mmol) of the black palladium powder obtained above, 1.2 mL (1.48 g, 7.5 mmol) of **2b**, 3.8 mL (5.08 g, 37.5 mmol) of trichlorosilane, and dodecane (0.25 mL, 0.19 g) as an internal standard under dry nitrogen at room temperature. The reaction was carried out at 100 °C for 8.5 h. The dechlorinated product **3b** (31%) was observed along with unreacted **2b** (69%) by GLC.

Catalytic Activity in Repeated Experiments for the Dechlorination of 2b by Trichlorosilane. In a 25 mL sealed stainless steel bomb were charged 1.0 mg (0.0045 mmol) of palladium diacetate, 0.69 mL (0.89 g, 4.5 mmol) of **2b**, 2.3 mL (3.05 g, 22.5 mmol) of trichlorosilane, and dodecane (0.25 mL, 0.19 g) as an internal standard under dry nitrogen at room temperature. The first reaction was carried out at 100 °C for 8.5 h. The dechlorinated products, **3b** (69%) and **4b** (16%), were observed along with unreacted **2b** (15%) by GLC. After all the volatile compounds in the bomb were distilled out under vacuum, the same amounts of **2b**, trichlorosilanes, and dodecane as above were charged into the reaction bomb with the palladium catalyst. The second reaction gave **3b** (36%) and unreacted **2b** (64%) in the analysis of GLC data, and the third reaction gave **3b** (27%) and unreacted **2b** (73%).

Acknowledgment. This research was supported financially by the Ministry of Science and Technology of Korea.

OM970490C

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