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HYDROGEN—CHLORINE EXCHANGE BETWEEN ORGANOSILICON HYDRIDES AND POLYCHLOROALKANES CATALYZED BY RUTHENIUM(II)-PHOSPHINE COMPLEXES

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Summary

Carbon tetrachloride, 1,1,1-trichloroethane, and 1,1,1,3-tetrachloroalkanes were selectively reduced by silicon hydrides to give chloroform, 1,1-dichloroethane, and 1,1,3-trichloroalkanes, respectively, in high yields in the presence of catalytic amounts of phosphine complexes of ruthenium(II) such as $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{RuHCl}(\text{PPh}_3)_3$, $\text{RuH}_2(\text{PPh}_3)_4$, and $\text{RuH}(\text{SiMe}_2\text{Cl})(\text{PPh}_3)_3$. Reactivities of a wide variety of silicon hydrides towards the dechlorination also were estimated. The catalytic cycle can be explained in terms of successive oxidative addition, reductive elimination, and hydrogen—halogen exchange on the ruthenium—phosphine complex.

Introduction

Hydrogen—halogen exchange reactions between organosilicon hydrides and alkyl halides have been investigated extensively in the presence of peroxides [1], palladium [2], iron complexes [3], and aluminum chloride [4]. Otherwise, amine [5] and thiols [6] were used as reducing agents for the selective reduction of polyhalo compounds in the presence of iron complexes.

Recently Sasson and Rempel reported [7] the selective hydrogen transfer hydrogenolysis of a 1,1,1,3-tetrachloro- to a 1,1,3-trichloroalkane with isopropanol in the presence of dichlorotris(triphenylphosphine)ruthenium(II) as part of their study of the addition of carbon tetrachloride to alkenes [8].

We have found that geminal organic polychlorides such as carbon tetrachloride, 1,1,1-trichloroethane, and 1,1,1,3-tetrachloroalkanes are readily reduced to the corresponding dechlorinated compounds in high yield by organosilicon hydrides when catalytic amounts of ruthenium(II)—phosphine complexes are used. In this

Table 1. REDUCTION OF POLYCHLOROALKANES WITH Et_3SiH^a CATALYZED BY $\text{RuCl}_2(\text{PPh}_3)_3$

Polychloroalkane (mmol.)	Catalyst mmol	Reaction Condition	Conv. ^b %	Product (glc yield, %) ^b
CCl_4 (21) ^c	0.027	Sealed tube 80°, 5hr.	100 ^d	CHCl_3 (100) ^d
CH_3CCl_3 (50)	0.05	Sealed tube 100° 10hr.	100	CH_3CHCl_2 (94)
CH_3CHCl_2 (25)	0.025	Sealed tube 100° 16hr.	34	$\text{C}_2\text{H}_5\text{Cl}$ (33)
$n\text{-C}_4\text{H}_9\text{CHClCH}_2\text{CCl}_3$ (10)	0.01	Reflux(Ar), 5hr.	41	$n\text{-C}_4\text{H}_9\text{CHClCH}_2\text{CHCl}_2$ (41)
$n\text{-C}_4\text{H}_9\text{CHClCH}_2\text{CCl}_3$ (50)	0.05	Sealed tube 100°, 14hr.	98	$n\text{-C}_4\text{H}_9\text{CHClCH}_2\text{CHCl}_2$ (92, isolated 84)
$n\text{-C}_5\text{H}_{11}\text{CHClCH}_2\text{CCl}_3$ (10)	0.01	Reflux(Ar), 5hr.	57	$n\text{-C}_5\text{H}_{11}\text{CHClCH}_2\text{CHCl}_2$ (57)
$n\text{-C}_5\text{H}_{11}\text{CHClCH}_2\text{CCl}_3$ (50)	0.05	Sealed tube 100°, 14hr.	98	$n\text{-C}_5\text{H}_{11}\text{CHClCH}_2\text{CHCl}_2$ (91, isolated 86)
$n\text{-C}_6\text{H}_{13}\text{CHClCH}_2\text{CCl}_3$ (50)	-----	Sealed tube 100° 14hr.	trace	$n\text{-C}_6\text{H}_{13}\text{CHClCH}_2\text{CHCl}_2$ (trace)
$n\text{-C}_6\text{H}_{13}\text{CHClCH}_2\text{CCl}_3$ (10)	0.01	Reflux(Ar), 5hr.	73	$n\text{-C}_6\text{H}_{13}\text{CHClCH}_2\text{CHCl}_2$ (73)
$n\text{-C}_6\text{H}_{13}\text{CHClCH}_2\text{CCl}_3$ (50)	0.05	Sealed tube 100°, 14hr.	93	$n\text{-C}_6\text{H}_{13}\text{CHClCH}_2\text{CHCl}_2$ (95, isolated 87)
$n\text{-C}_7\text{H}_{15}\text{CHClCH}_2\text{CCl}_3$ (50)	0.05	Sealed tube 100°, 14hr.	99	$n\text{-C}_7\text{H}_{15}\text{CHClCH}_2\text{CHCl}_2$ (94)
$n\text{-C}_{14}^{29}\text{H}_{29}\text{CHClCH}_2\text{CCl}_3$ (50)	0.05	Sealed tube 100°, 14hr.	92	$n\text{-C}_{14}^{29}\text{H}_{29}\text{CHClCH}_2\text{CHCl}_2$ (90, isolated 87 ^e)
$n\text{-C}_6\text{H}_{13}\text{CHClCH}_2\text{CHCl}_2$ (25)	0.025	Sealed tube 100°, 16hr.	42	$n\text{-C}_6\text{H}_{13}\text{CHClCH}_2\text{CH}_2\text{Cl}$ (38)

a, 20 mol% excess of triethylsilane was used. b, based on polychloroalkane. c, 9 mmol of triethylsilane was used. d, based on triethylsilane. e, crude yield.

paper we report the scope and limitations of these reactions and describe the mechanistic aspects of the catalytic cycle.

Results and discussion

The reaction of an excess of CCl_4 and triethylsilane in the presence of 0.3 mol% of $\text{RuCl}_2(\text{PPh}_3)_3$ in an evacuated sealed tube at 80°C for 5 h afforded chloroform and triethylchlorosilane quantitatively.

1,1,1-Trichloroethane reacted with triethylsilane (20 mol% excess) in the presence of 0.1 mol% of $\text{RuCl}_2(\text{PPh}_3)_3$ at 100°C (sealed tube) for 10 h to give a 94% yield of 1,1-dichloroethane and a 6% yield of ethyl chloride, and a quantitative yield of triethylchlorosilane. A series of 1,1,1,3-tetrachloroalkanes was treated with 20 mol% excess of triethylsilane in the presence of 0.1 mol% of $\text{RuCl}_2(\text{PPh}_3)_3$ under argon atmosphere at reflux for 5 h or in a sealed tube at 100°C for 14 h. GLC analyses indicated the formation of 1,1,3-trichloroalkanes and triethylchlorosilane in good yield, together with small amounts of 1,3-dichloroalkanes and monochloroalkanes. A similar reaction of 1,1,1,3-tetrachlorononane carried out without a catalyst afforded only a trace of 1,1,3-trichlorononane. Treatment of 1,1-dichloroethane and 1,1,3-trichlorononane with triethylsilane (20 mol% excess) in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$ (0.1 mol%) at 100°C for 16 h gave ethyl chloride (33%) and 1,3-dichlorononane (38%), respectively. Table 1 summarizes the reductions of polychloroalkanes with triethylsilane catalyzed by $\text{RuCl}_2(\text{PPh}_3)_3$.

Other ruthenium-phosphine complexes such as $\text{RuHCl}(\text{PPh}_3)_3$, $\text{RuH}_2(\text{PPh}_3)_4$ and $\text{RuH}(\text{SiMe}_2\text{Cl})(\text{PPh}_3)_3$ [9] also were found to be effective catalysts for the triethylsilane reduction reactions. Table 2 summarizes the yields of 1,1,3-tri-, 1,3-di- and mono-chlorononanes obtained when a variety of ruthenium(II)-

Table 2

REDUCTION OF 1,1,1,3-TETRACHLORONONANE WITH Et_3SiH ^{*1} CATALYZED

BY A VARIETY OF Ru-PHOSPHINE COMPLEXES AT 100°C

Ru-Phosphine Complex ^{*2}	Yields of Products(%) ^{*3}		
	$\text{C}_6\text{H}_{13}\text{CHClCH}_2\text{CHCl}_2$	$\text{C}_6\text{H}_{13}\text{CHClCH}_2\text{CH}_2\text{Cl}$	$\text{C}_9\text{H}_{19}\text{Cl}$
$\text{RuCl}_2(\text{PPh}_3)_3$	95	3	trace
$\text{RuHCl}(\text{PPh}_3)_3$	87	7	3
$\text{RuH}_2(\text{PPh}_3)_4$	90	4	3
$\text{RuH}(\text{SiMe}_2\text{Cl})(\text{PPh}_3)_3$	89	2	2

*1 20 mol% excess of triethylsilane was used.

*2 0.1 mol% of catalyst was used.

*3 GLC yield.

Table 3

REDUCTION OF 1,1,1,3-TETRACHLORONONANE WITH A VARIETY OF HYDROSILANES

CATALYZED BY $\text{RuCl}_2(\text{PPh}_3)_3$ ^{*1} AT 100°C

Hydrosilane ^{*2}	Conversion (%)	Yields of Products (%)		
		$\text{C}_6\text{H}_{13}\text{CHClCH}_2\text{CHCl}_2$	$\text{C}_6\text{H}_{13}\text{CHClCH}_2\text{CH}_2\text{Cl}$	$\text{C}_9\text{H}_{19}\text{Cl}$
Et_3SiH	99	95	3	trace
PhMe_2SiH	100	93	6	1
Me_2ClSiH	100	98	2	trace
MeCl_2SiH	59	57	1	trace
Cl_3SiH	3	3	0	0
$\text{Ph}(\text{MeO})_2\text{SiH}$	64	64	0	0
$(\text{EtO})_3\text{SiH}$	30	30	0	0
Ph_2SiH_2	100	76	19	4

*1 0.1 mol% of catalyst was used. *2 20 mol% excess of hydrosilane was used

phosphine catalysts were used in the reduction of 1,1,1,3-tetrachlorononane.



The reactivity of a series of silicon hydrides in the reduction of the tetrachlorononane catalyzed by $\text{RuCl}_2(\text{PPh}_3)_3$ was investigated (Table 3). Triethylsilane, phenyldimethylsilane, and dimethylchlorosilane reduced the tetrachloro compound to give 1,1,3-trichlorononane in high yield, together with small amounts of 1,3-di- and mono-chloro compounds. Methylchlorosilane, phenyldimethoxysilane, and triethoxysilane gave a moderate yield (30–64%) of 1,1,3-trichlorononane. A pale brown solid was isolated from the reaction mixture with methylchlorosilane and identified by means of its IR spectrum as $\text{RuH}(\text{SiMeCl}_2)(\text{PPh}_3)_3$ [9]. When trichlorosilane was used, only 3% yield of the reduced product was detected by GLC. A crystalline product was isolated from the reaction mixture and identified by IR as $\text{Ru}(\text{SiCl}_3)_2(\text{PPh}_3)_3$, a compound which had been reported by Svoboda, Řeřicha and Hetflejš [10]. The reaction of 20 mol% excess of diphenylsilane with the tetrachlorononane afforded a 76% yield of 1,1,3-trichloro, a 19% yield of 1,3-dichloro, and a 4% yield of monochloro compound.

The reactivity of silicon hydrides in this reduction follows the order: $\text{Ph}_2\text{SiH}_2 > \text{PhMe}_2\text{SiH} \approx \text{Me}_2\text{ClSiH} \approx \text{Et}_3\text{SiH} > \text{Ph}(\text{MeO})_2\text{SiH} > \text{MeCl}_2\text{SiH} > (\text{EtO})_3\text{SiH} \gg \text{Cl}_3\text{SiH}$.

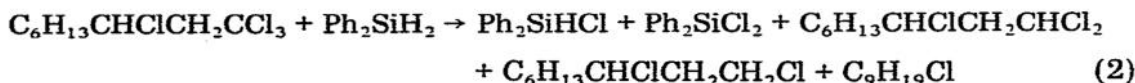
In Table 4 results of the Ph_2SiH_2 reductions of the tetrachlorononane are shown. As is apparent from Table 4, both hydrogen atoms of the dihydride are

Table 4

REDUCTION OF 1,1,1,3-TETRACHLORONONANE WITH Ph_2SiH_2 CATALYZED BY $\text{RuCl}_2(\text{PPh}_3)_3$ AT 100°C

Reactants mmol	$\left\{ \begin{array}{l} \text{Ph}_2\text{SiH}_2 \\ \text{Tetrachlorononane} \end{array} \right.$	30	15
		25	25
Products mmol (%)	$\left\{ \begin{array}{l} \text{Ph}_2\text{SiH}_2 \\ \text{Ph}_2\text{ClSiH} \\ \text{Ph}_2\text{SiCl}_2 \\ \text{C}_6\text{H}_{13}\text{CHClCH}_2\text{CCl}_3 \\ \text{C}_6\text{H}_{13}\text{CHClCH}_2\text{CHCl}_2 \\ \text{C}_6\text{H}_{13}\text{CHClCH}_2\text{CH}_2\text{Cl} \\ \text{C}_9\text{H}_{19}\text{Cl} \end{array} \right.$	4.2 (14)	trace
		18.6 (62)	3.3 (22)
		7.2 (24)	11.7 (78)
		0 (0)	0.8 (3)
		19.8 (76)	22.8 (89)
		4.8 (19)	1.5 (6)
		1.0 (4)	0.5 (2)

efficiently used for the reduction.



The treatment of the tetrachlorononane with triethyldeuteriosilane and diphenyldideuteriosilane in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$ afforded 1,1,3-trichlorononane which was not isotopically pure. According to mass spectroscopic and NMR analyses, it contained 62–64% (in the case of Et_3SiD) and 75–78% (in Ph_2SiD_2) of $\text{C}_6\text{H}_{13}\text{CHClCH}_2\text{CDCl}_2$, respectively.

Mechanistic aspects

Four different types of mechanisms are known for the silane reductions of alkyl halides: (a) intermolecular transfer of hydrogen from a silicon hydride to carbenium ions formed from alkyl halides and aluminum chloride [4], (b) a free radical chain mechanism initiated by benzoyl peroxide [1], (c) hydrogen–halogen exchange on the surface of palladium metal involving cleavage of silicon–hydrogen and carbon–halogen bonds [2], (d) a thermal process with reactive halides [11].

To explain and account for all the observations made in this study of the ruthenium(II)–phosphine complex-catalyzed reduction of polychloroalkanes by silicon hydrides, we propose an alternative mechanism as shown in Fig. 1.

In previous papers [9,12,13], we have reported the interaction of silicon hydrides with phosphine complexes of ruthenium(II). $\text{RuCl}_2(\text{PPh}_3)_3$ is reduced by Et_3SiH and PhMe_2SiH in solution to give $\text{RuHCl}(\text{PPh}_3)_3$. $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuHCl}(\text{PPh}_3)_3$ react with Me_2ClSiH , MeCl_2SiH , $\text{Ph}(\text{MeO})_2\text{SiH}$, $(\text{EtO})_3\text{SiH}$, and Ph_2SiH_2 in benzene to afford $\text{RuH}(\text{SiR}_3)(\text{PPh}_3)_3$. The reaction of $\text{RuH}_2(\text{PPh}_3)_4$

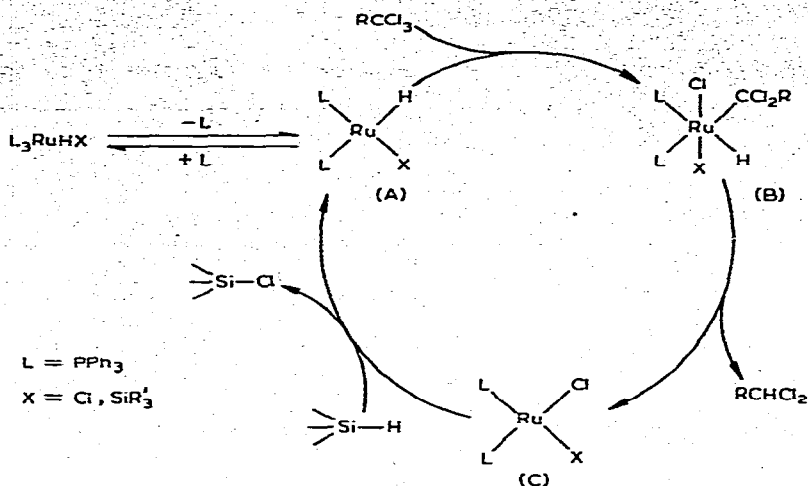
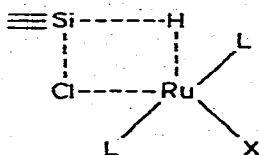
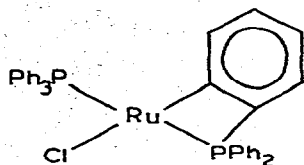


Fig. 1. Catalytic cycle of the reduction of a polychloroalkane with a hydrosilane.

with silicon hydrides gives $RuH_3(SiR_3)(PPh_3)_3$, which could lose H_2 to afford $RuH(SiR_3)(PPh_3)_3$. These five-coordinate, unsaturated complexes dissociate further to some extent to produce what might be 14-electron species, A [14]. Compound A is an active catalyst and could be converted into a complex, B, by oxidative addition of $RCCl_3$. The reaction presumably involves a homolytic cleavage of a carbon-halogen bond in the coordination sphere, as has been previously proposed for the addition of polyhalo compounds to olefins catalyzed by ruthenium(II) complexes [8,15]. The formation of six-coordinate d^4 complexes such as B also were suggested in $RuHCl(PPh_3)_3$ -catalyzed hydrogenation and isomerization of olefins [16,17] and reported in the oxidative addition of acyl chlorides to $RuH[Si(OMe)_3](PPh_3)_2$ [9]. The reductive elimination of $RCHCl_2$ from B gives a four-coordinate ruthenium halide complex, C. $RuCl_2(PPh_3)_2$ and $RuCl(SiR_3)(PPh_3)_2$ (C; $L = PPh_3$, $X = Cl, SiR_3$) can be easily reduced, in turn, to re-form the starting complex A by hydrogen-halogen exchange between $Ru-Cl$ and $Si-H$ bonds. For the interaction of the complex C and silicon hydride one may postulate a simple four center mechanism such as:



D-H exchange during the reactions of 1,1,1,3-tetrachlorononane with a deuteriosilane implies, to some extent, the interaction between the complex A and hydrocarbons present in the reaction media. In fact, $RuCl_2(PPh_3)_3$, when treated with triethyldeuteriosilane in benzene at room temperature was found to give a mixture of $RuDCl(PPh_3)_3$ and $RuHCl(PPh_3)_3$. It is not clear how and from where A abstracts hydrogen. Although the problem cannot be fully solved at this time, an intermediate D [18] certainly could contribute to activate the hydrogen-carbon bond.



(D)

Experimental

Materials. Hydrosilanes were prepared by known methods. Dichlorotris(triphenylphosphine)ruthenium was obtained by the reaction of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and triphenylphosphine in methanol [18]. Hydrido-chlorotris(triphenylphosphine)ruthenium was prepared by the reduction of $\text{RuCl}_2(\text{PPh}_3)_3$ with triethylsilane in benzene, as described in previous papers [9,10,14]. Dihydridotetrakis(triphenylphosphine)ruthenium was obtained by the reaction of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, triphenylphosphine, and sodium borohydride in ethanol [19]. Hydrido(dimethylchlorosilyl)tris(triphenylphosphine)ruthenium was prepared by the reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with Me_2ClSiH in benzene [9]. 1,1,1,3-Tetrachloroalkanes were obtained by the addition of CCl_4 to olefins in the presence of ruthenium(II)-phosphine complexes [7,8].

The reductions of 1,1,1,3-tetrachloroalkanes with silanes in the presence of ruthenium(II)-phosphine complexes

In a typical procedure, 1,1,1,3-tetrachlorononane (13.3 g, 50 mmol), Et_3SiH (6.96 g, 60 mmol), and $\text{RuCl}_2(\text{PPh}_3)_3$ (48 mg, 0.05 mmol) were introduced into a Carius tube, cooled in liquid nitrogen, degassed, sealed, and heated at 100°C , with stirring for 14 h. GLC analysis indicated that the resulting reaction mixture contained 1,1,1,3-tetrachlorononane (trace), 1,1,3-trichlorononane (48 mmol, 95%), 1,3-dichlorononane (1.5 mmol, 3%), monochlorononane (trace), Et_3SiH (5 mmol), and Et_3SiCl (54 mmol) (Silicone DC 550, 2 m, 158°C). The mixture was diluted with 30 ml of petroleum ether to precipitate solid materials, which were removed by filtration. The filtrate was concentrated by rotary evapora-

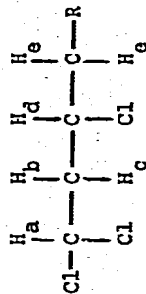
Table 6. RELATIVE INTENSITIES OF m/e 188 and 187 IN THE MASS SPECTRA OF 1,1,3-TRICHLORONONANE

Reducing Agent used	Intensities		Distribution of the mono-deuteriotrichlorononane (%)
	m/e 188	m/e 187	
Et_3SiH	8	100	0
Et_3SiD	188	100	64
Ph_2SiD_2	363	100	78

Table 5. PHYSICAL PROPERTIES OF 1,1,3-TRICHLOROALKANES

Compound	bp/mm (Lit.)	Analyses Found (Calcd.) (%)	NMR(100 MHz)	δ (ppm)
	(°C)	C H Cl		
$n\text{-C}_4\text{H}_9\text{CHClCH}_2\text{CHCl}_2$	89/10 (93/10)	41.84 (41.34) 6.48 (6.44)	51.13 (52.25)	5.90(d of d, 1H), 3.98(d of t, 1H), 2.46(d of d, 2H), 1.92-1.58(m, 2H), 1.58-0.80(m, 7H)
$n\text{-C}_5\text{H}_{11}\text{CHClCH}_2\text{CHCl}_2$	86/4	44.18 (44.17) 7.00 (6.95)	48.73 (48.89)	5.89(d of d, 1H), 3.99(d of t, 1H), 2.45(d of d, 2H), 1.90-1.58(m, 2H), 1.58-0.78(m, 9H)
$n\text{-C}_6\text{H}_{13}\text{CHClCH}_2\text{CHCl}_2$	102/5 (110/10)	46.95 (46.68) 7.39 (7.40)	46.19 (45.92)	5.88(d of d, 1H), 3.98(d of t, 1H), 2.45(d of d, 2H), 1.89-1.60(m, 2H), 1.60-0.79(m, 11H)
$n\text{-C}_7\text{H}_{15}\text{CHClCH}_2\text{CHCl}_2$	112/4	49.07 (48.90) 7.92 (7.80)	43.15 (43.30)	5.88(d of d, 1H), 3.98(d of t, 1H), 2.45(d of d, 2H), 1.88-1.57(m, 2H), 1.57-0.79(m, 13H)
$n\text{-C}_{14}\text{H}_{29}\text{CHClCH}_2\text{CHCl}_2$		59.93 (59.39) 9.79 (9.67)	30.44 (30.94)	5.93(d of d, 1H), 4.02(d of t, 1H), 2.47(d of d, 2H), 1.88-1.59(m, 2H), 1.59-1.12(m, 24H), 0.98(t, 3H)

* $J_{ab} = 6.0$ Hz, $J_{ac} = 7.0$ Hz, $J_{bd} = J_{cd} = 7.0$ Hz, $J_{de} = 13$ Hz



tion and distilled under reduced pressure to give 10.05 g (87% yield) of 1,1,3-trichlorononane, b.p. 100–102°C/5 mmHg. Physical properties of 1,1,3-trichloroalkanes obtained here are summarized in Table 5.

The reduction of 1,1,1,3-tetrachlorononane with diphenylsilane in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$. By a procedure similar to that described above, a mixture of 1,1,1,3-tetrachlorononane (6.65 g, 25 mmol), Ph_2SiH_2 (5.52 g, 30 mmol), and $\text{RuCl}_2(\text{PPh}_3)_3$ (24 mg, 0.025 mmol) was heated with stirring at 100°C for 14 h. The resulting reaction mixture was analyzed by GLC (Silicone DC 550, 2 m, 180°C) (see Table 4). Samples of 93% pure 1,3-dichlorononane and 97% pure diphenylchlorosilane were isolated by fractional distillation and preparative GLC and identified by NMR and mass spectroscopy.

1,3-Dichlorononane, $\text{C}_6\text{H}_{13}\text{CHClCH}_2\text{CH}_2\text{Cl}$, NMR (CCl_4) δ , ppm: 4.00 (m, 1 H), 3.63 (t, 2 H, J 6 Hz), 2.10 (q, 2 H, J 6 Hz), 2.0–0.7 (m, 13 H).

Diphenylchlorosilane, Ph_2SiHCl , NMR (CCl_4) δ , ppm: 7.70–7.03 (m, phenyl protons, 10 H), 5.62 (s, Si–H, 1 H).

Monochlorononane was identified by GC mass spectroscopy.

The reduction of 1,1,1,3-tetrachlorononane with triethyldeuteriosilane and diphenyldideuteriosilane. The reactions were run as described above. 1,1,3-Trichlorononane samples obtained by reduction with Et_3SiD and Ph_2SiD_2 in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$ were fractionally distilled. NMR spectra showed overlapping signals involving a doublet of doublets and a doublet (J 7 Hz) centered at δ 2.45 ppm. The integral ratios of two signals at δ 5.88 and 3.98 ppm were 0.38 and 0.25 for the trichlorononane from Et_3SiD and from Ph_2SiD_2 , respectively. The percentage of the monodeuterio compound in 1,1,3-trichlorononane also was determined by comparison of the relative intensities of m/e 188 and 187 ($M^+ - \text{C}_3\text{H}_7$) in the mass spectra. Table 6 shows the relative intensities of m/e 188 and 187 in the mass spectra of 1,1,3-trichlorononane obtained from the reduction with Et_3SiH , Et_3SiD , and Ph_2SiD_2 .

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