

## THE REACTIONS OF HYDROSILANES WITH TRIFLUOROPROPENE AND PENTAFLUOROSTYRENE CATALYZED BY RUTHENIUM, RHODIUM AND PALLADIUM COMPLEXES

IWAO OJIMA \*\*, TAKAMASA FUCHIKAMI and MOMOKO YATABE

*Sagami Chemical Research Center, Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229 (Japan)*

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### Summary

The reactions of hydrosilanes with trifluoropropene (TFP) and pentafluorostyrene (PFS) catalyzed by  $\text{Ru}_3(\text{CO})_{12}$  or  $\text{RhCl}(\text{PPh}_3)_3$  give  $\beta$ - $\text{R}_f$ -vinylsilane (1) and/or  $\beta$ - $\text{R}_f$ -ethylsilane (2) ( $\text{R}_f$  = perfluorocarbon group). The 1/2 ratio is highly dependent on the nature of hydrosilane used. The ruthenium catalyst favors the formation of 1 compared with the rhodium catalyst. Neither  $\alpha$ - $\text{R}_f$ -vinylsilane nor  $\alpha$ - $\text{R}_f$ -ethylsilane was formed at all. Possible mechanisms which can accommodate characteristic features of these reactions are discussed. The hydrosilylation of TFP with dichloromethylsilane catalyzed by  $\text{PdCl}_2(\text{PhCN})_2/2\text{PPh}_3$  gives the  $\alpha$ -adduct (9a) exclusively, and this is transformed to the corresponding dialkoxysilanes, silane diol, oligosilane diols and cyclic oligosiloxanes.

### Introduction

It has been shown that the hydrosilylation of fluorine-containing olefins is promoted by photoirradiation [1], radical initiators [2], or platinum catalysts [3]. The reported reactions afford terminal adducts exclusively in all cases. Among these reactions, the hydrosilylation of 3,3,3-trifluoropropene (TFP) with dichloromethylsilane, giving ( $\beta$ -trifluoromethylethyl)dichloromethylsilane, has been intensively studied in connection with the commercial production of "fluorosilicone". In the course of our study on the functionalizations of fluorine-containing olefins [4], which provide versatile synthetic building blocks, we were interested in the reaction of hydrosilanes with trifluoropropene (TFP) and pentafluorostyrene (PFS) in the presence of ruthenium, rhodium and palladium complexes since platinum had been the only transition metal used in the reaction of this type. We describe here our study on the reactions of a variety of hydrosilanes with TFP and PFS catalyzed by

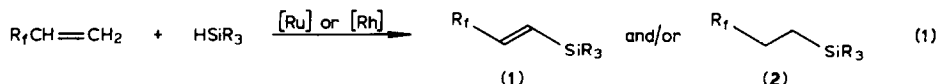
\* Present address: Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794, U.S.A.

$\text{Ru}_3(\text{CO})_{12}$ ,  $\text{RhCl}(\text{PPh}_3)_3$  and  $\text{PdCl}_2(\text{PhCN})_2/2\text{PPh}_3$ , which revealed remarkable effects of the catalyst species, as well as the nature of hydrosilane, on the features of the reaction: the results are in sharp contrast to the platinum catalyzed reaction [3].

## Results and discussion

### *The reactions of hydrosilanes with TFP and PFS catalyzed by ruthenium and rhodium complexes*

The ruthenium complex-catalyzed reactions were performed by using a variety of hydrosilanes at 70–150°C, which gave *trans*- $\beta$ - $\text{R}_f$ -vinylsilane (**1**) and/or  $\beta$ - $\text{R}_f$ -ethylsilane (**2**) (eq. 1). Results are listed in Table 1.



As Table 1 shows, the nature of the hydrosilane used exerts a remarkable influence on the selectivity of the reaction, especially when TFP was employed. For instance, the reaction of TFP with triethylsilane gave **1** exclusively, while that with triethoxysilane gave **2** as the sole adduct. The reactivity of dichloromethylsilane was very low, giving **2** as the predominant product, and it was found that the reaction with trichlorosilane did not proceed at all in spite of repeated runs under rather drastic conditions (150°C, 70 h). The reactions with PFS gave similar results, but the formation of **1** was considerably favored, especially for chlorohydrosilanes, in comparison with the case of TFP.

For the reactions of trialkyl- and phenyldialkylsilanes with styrenes, vinyl-naphthalene and allyl phenyl ether catalyzed by  $\text{Ru}_3(\text{CO})_{12}$ , Seki et al. reported the exclusive formation of the corresponding vinylsilanes [5]. Accordingly, the observed remarkable dependency of selectivity (**1** vs. **2**) on the nature of the hydrosilane used is noteworthy. Seki et al. also reported that the reaction of an electron deficient

TABLE 1

THE REACTIONS OF HYDROSILANES WITH TFP AND PFS CATALYZED BY  $\text{Ru}_3(\text{CO})_{12}$

Entry	Olefin	Hydrosilane	Conditions (°C/h)	Isolated yield(%) <sup>a</sup>	Product ratio <sup>b</sup> <b>1/2</b>
a	TFP	HSiEt <sub>3</sub>	70/6	78	100/0
b	TFP	HSiMe <sub>2</sub> Et	70/3	89	98/2
c	TFP	HSiMe <sub>2</sub> Ph	70/3	80	85/15
d	TFP	HSiMe <sub>2</sub> Cl	120/24	79	82/18
e	TFP	HSiMeCl <sub>2</sub>	120/70	11	22/78
f	TFP	HSiCl <sub>3</sub>	150/70	—	—
g	TFP	HSi(OEt) <sub>3</sub>	150/24	52	0/100
h	PFS	HSiEt <sub>3</sub>	70/18	92 <sup>c</sup>	100/0
i	PFS	HSiMe <sub>2</sub> Et	70/18	85 <sup>c</sup>	94/6
j	PFS	HSiMe <sub>2</sub> Ph	70/18	80 <sup>c</sup>	94/6
k	PFS	HSiMe <sub>2</sub> Cl	120/76	75 <sup>c</sup>	89/11
l	PFS	HSiMeCl <sub>2</sub>	120/48	60 <sup>c</sup>	58/42
m	PFS	HSiCl <sub>3</sub>	120/70	51 <sup>c</sup>	46/54

<sup>a</sup> Based on the hydrosilane used unless otherwise noted. <sup>b</sup> Determined by GLC and <sup>19</sup>F NMR analyses.

<sup>c</sup> Based on the hydrosilane consumed.

olefin, ethyl acrylate, with triethylsilane, catalyzed by  $\text{Ru}_3(\text{CO})_{12}$ , gave a mixture of ethyl  $\beta$ -triethylsilylacrylate (39%) and ethyl  $\beta$ -triethylsilylpropionate (12%) [6]. It should therefore be noted that a similar reaction with TFP gave ( $\beta$ -trifluoromethylvinyl)triethylsilane (**1a**) exclusively.

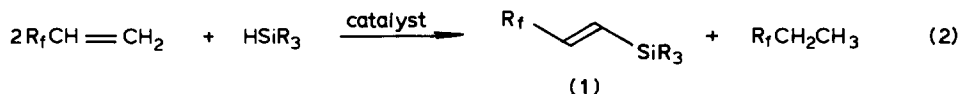
In a manner similar to the ruthenium complex catalyzed reactions, the reactions of hydrosilanes with TFP and PFS catalyzed by  $\text{RhCl}(\text{PPh}_3)_3$  were carried out. The results are listed in Table 2. As Table 2 shows, the 1/2 ratio is highly dependent on the nature of the hydrosilane used, and the dependency is more remarkable than that observed for the ruthenium complex catalyzed reactions. There is a clear difference in the 1/2 selectivity between chlorohydrosilanes and trialkyl- or phenyldialkylsilanes, viz., the first gave **2** as the sole product while the others gave a mixture of **1** and **2**.

It has been reported that the reactions of hydrosilanes with acrylonitrile gave branched adducts,  $\alpha$ -silylpropionitriles, exclusively except the case using trichlorosilane [7], and so the present results, giving only  $\beta$ -silyl products, **1** and/or **2**, form a sharp contrast to those for acrylonitrile.

#### *On the mechanism for the ruthenium and rhodium complex catalyzed reactions*

With regard to the mechanism of these reactions, we observed that an equi-molar amount of hydrogenated product ( $\text{R}_f\text{CH}_2\text{CH}_3$ ), relative to **1**, was formed, which was readily analyzed quantitatively, especially when PFS was employed (see Experimental).

Thus, the stoichiometry of the dehydrogenative silylation should be shown as follows:



For mechanistic considerations there are two possibilities, viz., (i) there are two

TABLE 2  
THE REACTIONS OF HYDROSILANES WITH TFP AND PFS CATALYZED BY  $\text{RhCl}(\text{PPh}_3)_3$

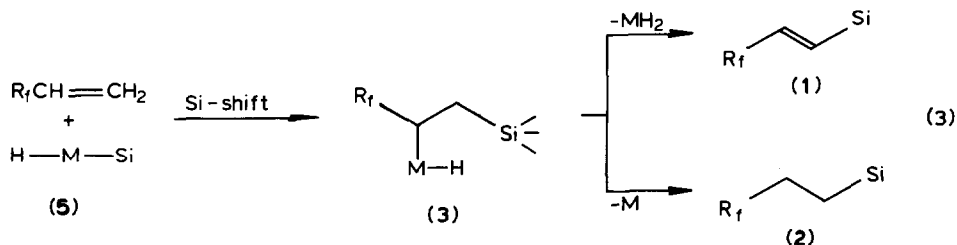
Entry	Olefin	Hydrosilane	Conditions (°C/h)	Isolated yield(%) <sup>a</sup>	Product ratio <sup>b</sup> 1/2
a	TFP	HSiEt <sub>3</sub>	70/6	77	87/13
b	TFP	HSiMe <sub>2</sub> Et	70/3	78	37/63
c	TFP	HSiMe <sub>2</sub> Ph	70/3	70	16/84
d	TFP	HSiMe <sub>2</sub> Cl	120/12	83	0/100
e	TFP	HSiMeCl <sub>2</sub>	120/12	85	0/100
f	TFP	HSiCl <sub>3</sub>	120/36	75	0/100
g	TFP	HSi(OEt) <sub>3</sub>	120/24	85	0/100
h	PFS	HSiEt <sub>3</sub>	70/18	91 <sup>c</sup>	89/11
i	PFS	HSiMe <sub>2</sub> Et	70/18	76 <sup>c</sup>	42/58
j	PFS	HSiMe <sub>2</sub> Ph	100/15	79 <sup>c</sup>	31/69
k	PFS	HSiMe <sub>2</sub> Cl	120/24	44 <sup>c</sup>	0/100
l	PFS	HSiMeCl <sub>2</sub>	120/24	72 <sup>c</sup>	0/100
m	PFS	HSiCl <sub>3</sub>	120/24	84 <sup>c</sup>	0/100

<sup>a</sup> Based on the hydrosilane used unless otherwise noted. <sup>b</sup> Determined by GLC and <sup>19</sup>F NMR analyses.

<sup>c</sup> Based on the hydrosilane consumed.

competing mechanisms, and one pathway yields **1** by dehydrogenative silylation while the other gives **2** by simple hydrosilylation, and (ii) there is a common intermediate, and the product distribution is dependent on the nature of the substituents.

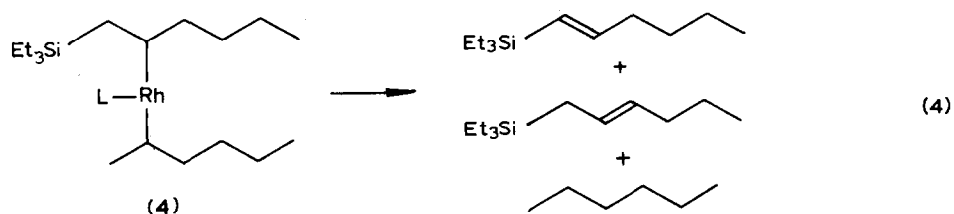
If we take the possibility (i), we should assume the initial silicon shift from the hydrosilane oxidative adduct, H-M-Si< (**5**), to form the  $\beta$ -silyl- $\alpha$ -R<sub>f</sub>-ethylmetal hydride (**3**), followed by  $\beta$ -hydride elimination or reductive elimination to rationalize the formation of **1** or **2** (eq. 3). As far as the hydrosilylation of *olefins* catalyzed by



Group VIII transition metals or metal complexes is concerned, the first silicon shift from the oxidative adduct (**5**) is unknown [8]. Besides this, if **2** is formed via simple hydrosilylation, the exclusive formation of  $\beta$ -adduct is hard to explain since  $\alpha$ -adduct is expected to be a rather preferable isomer, taking into account the strongly electron-withdrawing nature of the R<sub>f</sub> group and the well established mechanism for the hydrosilylation of olefins.

In fact, it has been reported that the hydrosilylation of styrene catalyzed by chloroplatinic acid gave a mixture of  $\alpha$ - and  $\beta$ -adducts, whereas the reaction of methyl acrylate, catalyzed by chloroplatinic acid, and the reaction of acrylonitrile, catalyzed by RhCl(PPh<sub>3</sub>)<sub>3</sub>, gave exclusively  $\alpha$ -adducts. Consequently, the possibility (i) seems to be inadequate to accommodate the observed results.

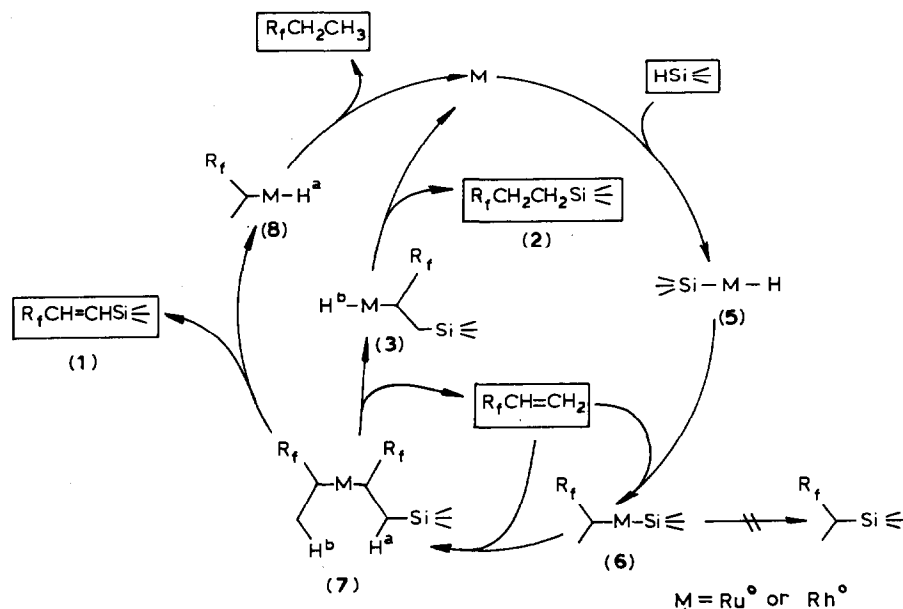
As for the mechanism of dehydrogenative silylation, giving vinylsilane, allylsilane and alkane, Millan et al. proposed [9] a dialkylrhodium intermediate (**4**) in their rhodium complex catalyzed reaction of triethylsilane with 1-hexene (eq. 4). For the



formation of 1-hexyltriethylsilane, Millan et al. proposed [9] the competitive hydrosilylation route since the exclusive formation of the straight chain adduct is normal for the rhodium complex catalyzed hydrosilylation of 1-hexene. However, in the case of TFP and PFS, the exclusive formation of the straight chain adduct (**2**) is unusual, as described above. By taking into account all of the characteristic features of the present reaction, we would like to propose the mechanism illustrated in Scheme 1. The proposed mechanism involves firstly a hydride shift from the oxidative adduct (**5**) to R<sub>f</sub>CH=CH<sub>2</sub>, giving the  $\alpha$ -R<sub>f</sub>-ethylmetal intermediate (**6**) (which does not undergo reductive elimination to give the  $\alpha$ -silyl adduct at all because of the strong coordination of another molecule of R<sub>f</sub>CH=CH<sub>2</sub>), followed

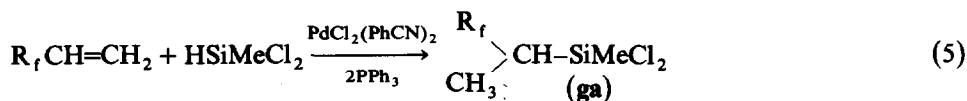
by the fast silicon shift from **6** to give **7**. When  $H^b$  is abstracted from **7**,  $\beta$ -silyl- $\alpha$ - $R_f$ -ethylmetal hydride (**3**) should be formed and, at the same time,  $R_fCH=CH_2$  should be regenerated, and the reductive elimination should give **2** as the apparent hydrosilylation product. On the other hand, when  $H^a$  is abstracted, **1** and the  $\alpha$ - $R_f$ -ethylmetal hydride (**8**) should be formed, and this undergoes reductive elimination to give the alkane,  $R_fCH_2CH_3$ , regenerating the active catalyst species,  $M$ .

SCHEME 1



*The reactions of hydrosilanes with TFP and PFS catalyzed by the palladium complex*

Attempted reactions of trialkylsilane, phenyldialkylsilane and chlorodimethylsilane with TFP and PFS catalyzed by  $PdCl_2(PhCN)_2/2PPh_3$  resulted in the recovery of TFP and the polymerization of PFS, and no adducts were obtained. The palladium complex catalyzed reaction of PFS with dichloromethylsilane and trichlorosilane gave only trace amounts of the  $\alpha$ -adducts (**9**), which were identified by  $^1H$  NMR spectroscopy. However, the hydrosilylation of TFP with dichloromethylsilane proceeded smoothly at  $100^\circ C$  to give ( $\alpha$ -trifluoromethylethyl)dichloromethylsilane (**9a**) in 88% yield. No straight chain adduct was formed at all. When 3,3,4,4,4-penta-



fluorobutene and dichloromethylsilane were employed, the reaction also gave the  $\alpha$ -adduct (**9b**) exclusively in 38% yield.

It is interesting to note that the palladium complex catalyzed reaction of TFP with trichlorosilane gave  $\beta$ -adduct (**2f**) as the predominant product (**2f/9c** = 92/8; by  $^{19}F$  NMR). Interpretation of the observed dramatic change in regioselectivity must await further study.

As the hydrosilylation of TFP, promoted by photoirradiation, radical initiators or platinum catalysts, gives the  $\beta$ -adduct as sole product [1-3], the present result, giving  $\alpha$ -adduct (**9**) exclusively, is unique.

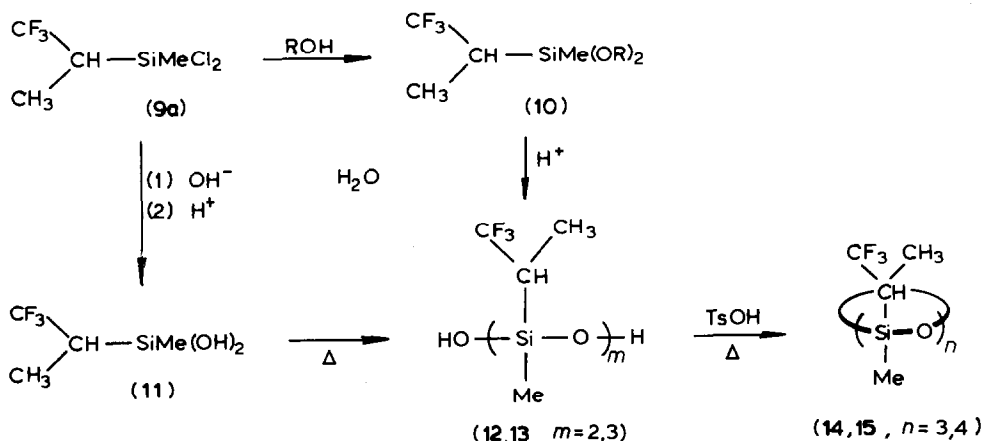
Since **9a** is a potent monomer for new fluorosilicones, we carried out alcoholysis, hydrolysis and oligosiloxane formation.

( $\alpha$ -Trifluoromethylethyl)diethoxymethylsilane (**10a**) was obtained in 82% yield by the direct ethanolysis of **9a**, while the corresponding dimethoxysilane (**10b**) was obtained in 63% yield by methanolysis in the presence of tributylamine. The direct methanolysis of **9a** gave **10b** in only low yield.

The hydrolysis of **9a** with 1 M NaOH in ether at 0°C gave ( $\alpha$ -trifluoromethylethyl)methylsilane diol (**11**) in 92% yield. The silane diol (**11**) was converted to a mixture of the corresponding disiloxane diol (**12**) (53%) and trisiloxane diol (**13**) (24%) simply by heating **11** at 120°C for 2 h, followed by distillation under reduced pressure. The corresponding cyclic trisiloxane (**14**) and cyclic tetrasiloxane (**15**) were obtained by heating a mixture of **12** and **13** with a catalytic amount of *p*-toluenesulfonic acid in benzene, removing the generated water as the azeotrope.

The transformations of **9a** to **10-15** are illustrated in Scheme 2.

SCHEME 2



## Experimental

B.ps. and m.ps. are uncorrected.  $^1\text{H}$  NMR spectra were recorded on Varian EM-360, EM-390, or XL-100-15A spectrometers, with tetramethylsilane as the internal standard.  $^{19}\text{F}$  NMR spectra were measured with Hitachi R-20B or Varian XL-100-15A spectrometers, with fluorotrichloromethane as the internal standard. Chemical shifts ( $\delta$ ), in ppm from the internal standard, are given as positive values for downfield shifts in all cases. IR spectra were recorded on a JASCO A-202 spectrophotometer by using samples as neat liquids or in KBr disks. Mass spectra were measured with a Hitachi RMU-6MG spectrometer at 70 eV. Analytical GLC was carried out with a Shimadzu GC-7A using columns packed with 30% SE-30 and DC-550 on Uniport B. Preparative GLC was performed with a Varian Aerograph

Model 920 using a column packed with 30% SE-30. Molecular weights were determined ebullioscopically with a Hitachi-Perkin-Elmer Model 115. 3,3,3-Trifluoropropene (TFP) and pentafluorostyrene (PFS) were commercially available from Japan Halon Co. and Yarsley Res. Lab., respectively, and used as purchased.  $\text{Ru}_3(\text{CO})_{12}$  was purchased from Strem Chemicals, Inc.  $\text{RhCl}(\text{PPh}_3)_3$  [10] and  $\text{PdCl}_2(\text{PhCN})_2$  [11] were prepared by literature methods. Chlorohydrosilanes were commercially available and other hydrosilanes were prepared by known methods.

*Reaction of hydrosilane with trifluoropropene catalyzed by  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{RhCl}(\text{PPh}_3)_3$*

A typical procedure is described for the reaction of triethylsilane with TFP catalyzed by  $\text{Ru}_3(\text{CO})_{12}$ .

In a 50 ml stainless steel autoclave was placed a mixture of  $\text{Ru}_3(\text{CO})_{12}$  (23.6 mg,  $3.7 \times 10^{-2}$  mmol) and triethylsilane (1.20 g, 10.7 mmol). The autoclave was cooled with liquid nitrogen and was degassed. Then, TFP (480 ml, 21.4 mmol) was introduced to the autoclave from a lecture bottle. The autoclave was heated at 70°C with stirring for 6 h. The pressure decreased as the reaction proceeded. After cooling to 0°C and depressuring, the autoclave was opened and the reaction mixture was submitted to a fractional distillation under reduced pressure to give ( $\beta$ -trifluoromethylvinyl)triethylsilane (**1a**) (1.63 g, 78% yield) as a colorless liquid: b.p. 88°C/80 Torr.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.50–1.10 (m, 15 H), 6.00 (d of q,  $J = 19.3$  Hz, 5.6 Hz, 1 H) and 6.52 (d of q,  $J = 19.3$  Hz, 1.8 Hz, 1H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta -67.1$  (d of d,  $J = 5.6$  Hz, 1.8 Hz). IR (neat): 1635, 1470, 1460, 1415, 1310, 1285, 1240, 1130, 1020, 990, 850, 790 and 730  $\text{cm}^{-1}$ . Mass spectrum,  $m/e$  (% rel. inten.): 181 ( $M^+ - 29$ ) (62), 153 (100), 125 (35), 105 (17), 85 (15), 77 (16), 57 (14) and 41 (17). (Found: C, 51.40; H, 8.15.  $\text{C}_9\text{H}_{17}\text{F}_3\text{Si}$  calcd.: C, 51.50; H, 8.21%).

In a similar manner, **1b–1e** and **2a–2g** were obtained (see, Tables 1 and 2). When a mixture of **1** and **2** was produced, the two products were separated and isolated by preparative GLC.

**1b**: b.p. 113°C/760 Torr.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.05 (6 H), 0.40–1.10 (m, 5H), 5.28 (d of q,  $J = 19.1$  Hz, 5.6 Hz, 1 H) and 6.57 (d of q,  $J = 19.1$  Hz, 1.8 Hz, 1H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta -67.2$  (d of d,  $J = 5.6$  Hz, 1.8 Hz). IR (neat): 1640, 1320, 1290, 1260, 1240, 1130, 990, 860 and 840  $\text{cm}^{-1}$ . Mass spectrum,  $m/e$  (% rel. inten.): 153 ( $M^+ - 29$ ) (100), 139 (45), 81 (13), 77 (21), 75 (25), 59 (36) and 57 (11). (Found: C, 46.09; H, 7.28.  $\text{C}_7\text{H}_{13}\text{F}_3\text{Si}$  calcd.: C, 46.13; H, 7.19%).

**1c**: b.p. 108–110°C/40 Torr.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.43 (s, 6 H), 6.02 (d of q,  $J = 18.9$  Hz, 5.6 Hz, 1 H), 6.71 (d of q,  $J = 18.9$  Hz, 1.9 Hz, 1 H) and 7.20–7.60 (m, 5H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta -67.1$  (d of d,  $J = 5.6$  Hz, 1.9 Hz). IR (neat): 1630, 1425, 1310, 1280, 1250, 1230, 1120, 985, 850, 840, 830, 790, 730 and 700  $\text{cm}^{-1}$ . Mass spectrum,  $m/e$  (% rel. inten.): 215 ( $M^+ - 15$ ) (100), 135 (46), 134 (54), 133 (68), 121 (51), 77 (100), 47 (18) and 43 (22). (Found: C, 57.08; H, 5.68.  $\text{C}_{11}\text{H}_{13}\text{F}_3\text{Si}$  calcd.: C, 57.37; H, 5.69%).

**1d**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.51 (s, 3H), 6.24 (d of q,  $J = 19.2$  Hz, 5.6 Hz, 1 H) and 6.61 (d of q,  $J = 19.2$  Hz, 1.8 Hz, 1 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta -67.5$  (d of d,  $J = 5.6$  Hz, 1.8 Hz).

**1e**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.94 (s, 3H), 6.37 (d of q,  $J = 18$  Hz, 3.8 Hz, 1 H) and 6.68 (d,  $J = 18$  Hz, 1 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta -67.4$  (d,  $J = 3.8$  Hz).

**2a**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.50–1.10 (m, 17 H) and 1.50–2.20 (m, 2 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta -69.6$  (t,  $J = 10.6$  Hz).

**2b:**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.06 (s, 6 H), 0.40–1.10 (m, 7H) and 1.60–2.30 (m, 2H).  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -69.4 (t,  $J = 10.5$  Hz).

**2c:**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.32 (s, 6 H), 0.80–1.10 (m, 2H), 1.60–2.30 (m, 2 H) and 7.20–7.60 (m, 5 H).  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -69.3 (t,  $J = 10.2$  Hz).

**2d:** b.p. 117–118°C/760 Torr.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.46 (s, 6 H), 0.90–1.30 (m, 2 H) and 1.90–2.50 (m, 2 H).  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -69.0 (t,  $J = 10.3$  Hz).

**2e:** b.p. 120–123°C/760 Torr.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.85 (s, 3 H), 1.20–1.50 (m, 2 H) and 2.00–2.60 (m, 2 H).  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -69.2 (t,  $J = 10.2$  Hz).

**2f:** b.p. 111–112°C/760 Torr.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.60 (m, 2 H) and 2.40 (m, 2 H).  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -68.9 (t,  $J = 10$  Hz).

**2g:**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.82 (m, 2 H), 1.23 (t,  $J = 7$  Hz, 9 H), 2.10 (m, 2 H) and 3.82 (q,  $J = 7$  Hz, 6 H).  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -68.9 (t,  $J = 10.6$  Hz).

### *Reactions of hydrosilanes with pentafluorostyrene (PFS) catalyzed by $\text{Ru}_3(\text{CO})_{12}$ and $\text{RhCl}(\text{PPh}_3)_3$*

A typical procedure is described for the reaction of triethylsilane with PFS catalyzed by  $\text{RhCl}(\text{PPh}_3)_3$ .

A mixture of  $\text{RhCl}(\text{PPh}_3)_3$  (46.2 mg,  $5.0 \times 10^{-2}$  mmol), triethylsilane (580 mg, 5.0 mmol) and PFS (971 mg, 5.0 mmol) was sealed in a 10 ml pyrex tube under argon at ambient temperature, and heated at 70°C with stirring for 18 h. After cooling to room temperature, the pyrex tube was opened. The GLC analysis of the reaction mixture revealed that the **1h**/**2h** ratio was 89/11. Then, the reaction mixture was distilled under reduced pressure to give a mixture of ( $\beta$ -pentafluorophenylvinyl)triethylsilane (**1h**) and ( $\beta$ -pentafluorophenylethyl)triethylsilane (**2h**) as the fraction which boiled at 88°C/4 Torr. The mixture of **1h** and **2h** thus obtained was submitted to preparative GLC and **1h** (662 mg, 81% yield) and **2h** (81.8 mg, 10% yield) were isolated.

**1h:** b.p. 94.5°C/4 Torr. (determined for the sample obtained in the ruthenium complex-catalyzed reaction).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.46–1.09 (m, 15 H) and 6.72 (s, 2 H).  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -164.0 (m, 2 F), -157.2 (t,  $J = 20$  Hz, 1 F) and -145.1 (m, 2 F). IR (neat): 1650, 1520, 1500, 1000, 960, 820, 750, 740 and 730  $\text{cm}^{-1}$ . Mass spectrum,  $m/e$  (% rel. inten.): 279 ( $M^+ - 29$ ) (55), 251 (100), 223 (57), 217 (24), 105 (24) and 59 (36). (Found: C, 54.55; H, 5.54.  $\text{C}_{14}\text{H}_{17}\text{F}_5\text{Si}$  calcd.: C, 54.53; H, 5.56%).

**2h:**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.40–1.20 (m, 17 H) and 2.68 (m, 2 H).  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -164.1 (m, 2 F), -159.8 (t,  $J = 20$  Hz, 1 F) and -145.2 (m, 2 F).

The ruthenium complex catalyzed reaction was carried out in a similar manner. A mixture of  $\text{Ru}_3(\text{CO})_{12}$  (10.7 mg,  $1.6 \times 10^{-2}$  mmol), PFS (970 mg, 5.0 mmol) and triethylsilane (580 mg, 5.0 mmol) was heated at 70°C with stirring for 18 h. The GLC analysis of the reaction mixture revealed the quantitative formation of **1h** (2.5 mmol). The  $^1\text{H NMR}$  analysis of the reaction mixture showed that a half of the added triethylsilane (2.5 mmol) was recovered unchanged and an equimolar amount of ethylpentafluorobenzene (2.5 mmol) was formed:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) for the reaction mixture:  $\delta$  0.20–1.30 (m, 30 H) ( $\text{SiCH}_2\text{CH}_3$ ), 1.20 (t,  $J = 7$  Hz, 3 H) ( $\text{C}_6\text{F}_5\text{CH}_2\text{CH}_3$ ), 2.69 (bq,  $J = 7$  Hz, 2 H) ( $\text{C}_6\text{F}_5\text{CH}_2\text{CH}_3$ ), 3.57 (septet,  $J = 3$  Hz, 1 H) ( $\text{SiH}$ ) and 6.72 (s, 2 H) ( $\text{C}_6\text{F}_5\text{CH}=\text{CHSi}$ ). Then, the reaction mixture was distilled under reduced pressure to give **1h** as colorless liquid (704 mg, 92% yield) b.p. 94.5°C/4 Torr.



Similarly, the formation of the ethylpentafluorobenzene related to **1** was checked by the  $^1\text{H}$  NMR of the reaction mixture for other cases.

**1i:** b.p.  $96^\circ\text{C}/18$  Torr.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.05 (s, 6 H), 0.48–1.09 (m, 5 H) and 6.74 (s, 2 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -164.1 (m, 2 F), -157.0 (t,  $J = 20$  Hz, 1 F) and -145.1 (m, 2 F). IR (neat): 1650, 1520, 1500, 1000, 960 and  $840\text{ cm}^{-1}$ . Mass spectrum,  $m/e$  (% rel. inten.): 251 ( $M^+ - 29$ ) (76), 237 (24), 155 (20), 77 (50) and 59 (100). (Found: C, 51.31; H, 4.75.  $\text{C}_{12}\text{H}_{13}\text{F}_5\text{Si}$  calcd.: C, 51.42; H, 4.67%).

**1j:** b.p.  $117^\circ\text{C}/3$  Torr.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.44 (s, 6 H), 6.77 (d,  $J = 19$  Hz, 1 H), 6.88 (d,  $J = 19$  Hz, 1 H) and 7.26–7.59 (m, 5 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -163.8 (m, 2 F), -156.5 (t,  $J = 20$  Hz, 1 F) and -144.7 (m, 2 F). IR (neat): 1650, 1520, 1500, 1000, 960, 850 and  $835\text{ cm}^{-1}$ . Mass spectrum,  $m/e$  (% rel. inten.): 313 ( $M^+ - 15$ ) (18), 271 (59), 232 (39), 193 (55), 139 (32), 135 (89), 121 (100), 120 (32), 105 (38), 77 (66) and 43 (39). (Found: C, 58.47; H, 4.01.  $\text{C}_{16}\text{H}_{13}\text{F}_5\text{Si}$  calcd.: C, 58.53; H, 3.99%).

**1k:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.49 (s, 6 H), 6.74 (d,  $J = 20$  Hz, 1 H) and 6.90 (d,  $J = 20$  Hz, 1 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -163.4 (m, 2 F), -155.0 (t,  $J = 20$  Hz, 1 F) and -144.0 (m, 2 F).

**1l:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.50 (s, 3 H), 6.74 (d,  $J = 20$  Hz, 1 H) and 6.92 (d,  $J = 20$  Hz, 1 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -163.1 (m, 2 F), -154.9 (t,  $J = 20$  Hz, 1 F) and -143.9 (m, 2 F).

**1m:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.80 (d,  $J = 19$  Hz, 1 H) and 7.26 (d,  $J = 19$  Hz, 1 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -162.2 (m, 2 F), -151.5 (t,  $J = 20$  Hz, 1 F) and -142.0 (m, 2 F).

**2i:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.15 (s, 6 H), 0.40–1.10 (m, 7 H) and 2.69 (m, 2 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -146.2 (m, 2 F), -159.8 (t,  $J = 21$  Hz, 1 F) and -164.0 (m, 2 F).

**2j:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.32 (s, 6 H), 1.08 (m, 2 H), 2.69 (m, 2 H) and 7.27–7.66 (m, 5 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -164.0 (m, 2 F), -159.7 (t,  $J = 21$  Hz, 1 F) and -145.8 (m, 2 F).

**2k:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): b.p.  $102^\circ\text{C}/19$  Torr.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.44 (s, 6 H), 1.15 (m, 2 H) and 2.76 (m, 2 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -163.5 (m, 2 F), -158.7 (t,  $J = 20$  Hz, 1 F) and -145.5 (m, 2 F). Mass spectrum,  $m/e$  (% rel. inten.): 290 ( $M^+ + 2$ ) (1.1), 288 ( $M^+$ ) (3.5), 273 (11), 257 (28), 151 (15), 137 (27), 133 (34), 95 (24), 93 (67), 81 (25), 77 (100), 73 (12) and 47 (10).

**2l:** b.p.  $113^\circ\text{C}/21$  Torr.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.79 (s, 3 H), 1.00–1.55 (m, 2 H) and 2.60–3.02 (m, 2 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -163.1 (m, 2 F), -157.9 (t,  $J = 20$  Hz, 1 F) and -145.0 (m, 2 F). Mass spectrum,  $m/e$  (% rel. inten.): 310 ( $M^+ + 2$ ) (1.4), 308 ( $M^+$ ) (2.1), 276 (20), 182 (8), 181 (100), 176 (6), 137 (8), 115 (6), 113 (9) and 81 (15).

**2m:** b.p.  $93^\circ\text{C}/23$  Torr.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.66 (m, 2 H) and 2.96 (m, 2 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -162.8 (m, 2 F), -156.9 (t,  $J = 20$  Hz, 1 F) and -144.5 (m, 2 F). Mass spectrum,  $m/e$  (% rel. inten.): 334 ( $M^+ + 6$ ) (1.8), 332 ( $M^+ + 4$ ) (12.0), 330 ( $M^+ + 2$ ) (33.4), 328 ( $M^+$ ) (34.3), 294 (14), 292 (20), 182 (30), 181 (100), 176 (12), 175 (69), 135 (20) and 133 (21).

*Hydrosilylation of trifluoropropene (TFP) with dichloromethylsilane catalyzed by  $\text{PdCl}_2(\text{PhCN})_2/2\text{PPPh}_3$*

In a 200 ml stainless steel autoclave was placed a mixture of  $\text{PdCl}_2(\text{PhCN})_2$  (192 mg, 0.50 mmol), triphenylphosphine (262 mg, 1.00 mmol), and dichloromethylsilane

(10.3 g, 89.7 mmol) and TFP (12.8 g, 133 mmol) was introduced in a manner similar to that described for the ruthenium complex-catalyzed reaction. The autoclave was heated at 100°C for 14 h. Distillation of the reaction mixture gave ( $\alpha$ -trifluoromethylethyl)dichloromethylsilane (**9a**) as a colorless liquid (16.6 g, 88%): b.p. 112–113°C/760 Torr.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.89 (q,  $J = 0.9$  Hz, 3 H), 1.36 (d,  $J = 7$  Hz, 3 H) and 2.90 (m, 1 H).  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -62.4 (d of q,  $J = 11$  Hz, 0.9 Hz). IR (neat): 1330, 1250, 1170, 1120, 1060, 800 and 550  $\text{cm}^{-1}$ . Mass spectrum,  $m/e$  (% rel. inten.): 115 (18), 113 (26), 78 (100), 77 (64), 63 (15), 59 (22) and 39 (10); at 14 eV, the fragment peaks 197 [ $(M^+ + 2) - 15$ ] and 195 ( $M^+ - 15$ ) were detected. (Found: C, 22.86; H, 3.24.  $\text{C}_4\text{H}_7\text{F}_3\text{Cl}_2\text{Si}$  calcd.: C, 22.76; H, 3.34%).

Similarly, the hydrosilylation of TFP (20.5 mmol) with trichlorosilane (12.1 mmol), catalyzed by the palladium complex, was carried out (120°C, 27 h), to give a mixture of ( $\beta$ -trifluoromethylethyl)trichlorosilane (**2f**) and ( $\alpha$ -trifluoromethylethyl)trichlorosilane (**9c**) in 43% yield: b.p. 106–108°C/760 Torr. The  $^{19}\text{F NMR}$  analysis of the mixture showed that the **2f/9c** ratio was 92/8.

**9c**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.44 (d,  $J = 7.6$  Hz, 3 H) and 2.00–2.50 (m, 1 H).  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -62.3 (d,  $J = 10.1$  Hz).

The hydrosilylation of 3,3,4,4,4-pentafluorobutene (20.5 mmol) with dichloromethylsilane (10.3 mmol), catalyzed by the palladium complex (0.10 mmol) was carried out (100°C, 14 h) in a manner similar to that described above, and distillation of the reaction mixture gave [ $\alpha$ -(2,2,3,3,3-pentafluoroethyl)ethyl]dichloromethylsilane (**9b**) as a colorless liquid (1.03 g, 38% yield): b.p. 130°C/760 Torr.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.91 (d,  $J = 2$  Hz, 3 H), 1.37 (d of d,  $J = 7.5$  Hz, 1 H).  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -114.5 (d of d,  $J = 274$  Hz, 28 Hz, 1 F), -103.0 (d of d of q,  $J = 274$  Hz, 7.5 Hz, 2.5 Hz, 1 F) and -82.9 (d,  $J = 2.5$  Hz, 3 F). IR (neat): 1200, 1140, 1050, 1030, 1010, 820, 800 and 500  $\text{cm}^{-1}$ . Mass spectrum,  $m/e$  (% rel. inten.): 128 (185), 117 (35), 115 (71), 113 (100), 109 (66), 97 (42), 89 (50), 78 (42), 77 (50), 63 (49), 59 (100) and 39 (39).

#### *Alcoholysis of ( $\alpha$ -trifluoromethylethyl)dichloromethylsilane (9a)*

(A) To cooled absolute ethanol (1.8 g, 39.2 mmol) was added, dropwise, **9a** (2.07 g, 9.8 mmol) at 0°C with stirring. The stirring was continued for 4.5 h, with a continuous bubbling of dry argon gas into the mixture. Then the reaction mixture was distilled under reduced pressure to give ( $\alpha$ -trifluoromethylethyl)diethoxymethylsilane (**10a**) as a colorless liquid (1.86 g, 82% yield): b.p. 102–103°C/150 Torr.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.20 (s, 3H), 1.16 (d,  $J = 7$  Hz, 3 H), 1.18 (t,  $J = 7$  Hz, 6H), 1.66 (m, 1H) and 3.75 (q,  $J = 7$  Hz, 4 H).  $^{19}\text{F NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  -62.7 (d,  $J = 12$  Hz). IR (neat): 1340, 1250, 1170, 1110, 1090, 1055 and 770  $\text{cm}^{-1}$ . Mass spectrum,  $m/e$  (% rel. inten.): 137 (16), 134 (11), 133 (100), 125 (15), 107 (30), 105 (23), 97 (44), 89 (27), 79 (59), 78 (40) and 77 (68). (Found: C, 41.72; H, 7.65.  $\text{C}_8\text{H}_{17}\text{F}_3\text{O}_2\text{Si}$  calcd.: C, 41.72; H, 7.44%).

(B) To a cooled mixture of absolute methanol (1.58 g, 4.94 mmol) and tributylamine (2.67 g, 14.4 mmol) in dry ether (7 ml) was added dropwise **9a** (1.32 g, 6.26 mmol) at 0°C and the mixture was stirred for 1 h. Then, all of the volatile materials were collected in a trap, cooled in a dry ice-acetone bath, under reduced pressure (ca. 1 Torr). After the ether had been removed, the residue was distilled under reduced pressure to give ( $\alpha$ -trifluoromethylethyl)dimethoxymethylsilane (**10b**) as a colorless liquid (759 mg, 60% yield): b.p. 75–77°C/150 Torr.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$

0.15 (s, 3 H), 1.12 (d,  $J = 7$  Hz, 3 H), 1.65 (m, 1 H) and 3.50 (s, 6H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta -62.9$  (d,  $J = 12.5$  Hz). IR (neat): 1340, 1250, 1230, 1160, 1100, 1050, 1020, 840 and  $780\text{ cm}^{-1}$ . Mass spectrum,  $m/e$  (% rel. inten.): 125 (32), 109 (19), 105 (100), 93 (33), 79 (18), 78 (70), 77 (31), 75 (61), 63 (15) and 59 (17). (Found: C, 35.95; H, 6.41.  $\text{C}_6\text{H}_{13}\text{F}_3\text{O}_2\text{Si}$  calcd.: C, 35.63; H, 6.48%).

#### *Hydrolysis of ( $\alpha$ -trifluoromethylethyl)dichloromethylsilane (9a)*

To a cooled binary solution of 1 *M* sodium hydroxide (15 ml) and ether (15 ml) was added **9a** (1.27 g, 6.0 mmol) at  $0^\circ\text{C}$  with stirring, and the stirring was continued for 30 min. Then 1 *M* hydrochloric acid (4 ml) was added to the reaction mixture and the ether layer was separated and dried over anhydrous sodium sulfate. ( $\alpha$ -Trifluoromethylethyl)methylsilane diol (**11**) was precipitated as a white solid when hexane was added to the ether solution: 960 mg (92% yield), m.p.  $56\text{--}59^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.27 (bs, 3 H), 1.20 (bs,  $J = 7$  Hz, 3 H), 1.60 (m, 1 H) and 4.04 (bs, 2 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta -62.5$  (d,  $J = 12$  Hz). IR (KBr): 3300, 3000, 1480, 1460, 1395, 1335, 1250, 1165, 1105, 1055, 1020, 980, 920, 890, 840, 785, 750, 725, 680 and  $670\text{ cm}^{-1}$ . Mass spectrum,  $m/e$  (% rel. inten.): 157 (100), 137 (29), 78 (97), 77 (52) and 59 (40).

After **11** (1.14 g, 6.55 mmol) had been heated at  $120^\circ\text{C}$  for 2 h, the reaction mixture was distilled under reduced pressure to give 1,3-bis[( $\alpha$ -trifluoromethylethyl)methyl]disiloxane-1,3-diol (**12**) (576 mg, 53%) and 1,3,5-tris[( $\alpha$ -trifluoromethylethyl)methyl]trisiloxane-1,5-diol (**13**) (259 mg, 24% yield). The pot residue (200 mg, oil) was expected to be a mixture of poly[( $\alpha$ -trifluoromethylethyl)methyl]polysiloxane- $\alpha,\omega$ -diols, but further identification was not done.

**12**: b.p.  $117\text{--}119^\circ\text{C}/19$  Torr.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.22 (bs, 6 H), 1.14 (d,  $J = 7$  Hz, 6 H), 1.57 (m, 2 H) and 3.70 (bs, 2 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta -62.6$  (m). IR (neat): 3680, 3370, 3000, 1470, 1460, 1410, 1390, 1335, 1250, 1160, 1090, 1020, 970, 890, 785, 680 and  $645\text{ cm}^{-1}$ . Mass spectrum,  $m/e$  (% rel. inten.): 159 (16), 157 (21), 155 (100), 137 (65), 78 (56) and 77 (29). (Found: C, 28.95; H, 4.89.  $\text{C}_8\text{H}_{16}\text{F}_6\text{O}_3\text{Si}_2$  calcd.: C, 29.08; H, 4.88%).

**13**: b.p.  $146\text{--}150^\circ\text{C}/18$  Torr.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.22 (bs, 9 H), 1.14 (bd,  $J = 7$  Hz, 9 H), 1.60 (m, 3 H) and 2.8 (bs, 2 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta -62.6$  (m). IR (neat): 3690, 3350, 3000, 1470, 1460, 1410, 1390, 1325, 1250, 1160, 1090, 1020, 970, 890, 840, 785, 695 and  $640\text{ cm}^{-1}$ . Mass spectrum,  $m/e$  (% rel. inten.): 219 (12), 217 (17), 215 (100), 213 (15), 78 (30) and 77 (12). (Found: C, 29.38; H, 4.81.  $\text{C}_{12}\text{H}_{23}\text{F}_9\text{O}_4\text{Si}_3$  calcd.: C, 29.62; H, 4.76%).

#### *Formation of cyclic oligosiloxanes*

To a mixture of **12** and **13** (3.04 g,  $\text{12/13} = 2/1$ ) in benzene (20 ml) was added *p*-toluenesulfonic acid (50 mg, 0.29 mmol), and the mixture was heated under reflux for 40 h with a Dean-Stark separator until the generation of water ceased. Then, the reaction mixture was washed with water, dried over anhydrous sodium sulfate and submitted to distillation under reduced pressure, to give cyclic tris[( $\alpha$ -trifluoromethylethyl)methyl]trisiloxane (**14**) (490 mg) and cyclic tetrakis[( $\alpha$ -trifluoromethylethyl)methyl]tetrasiloxane (**15**) (1.05 g).

**14**: b.p.  $67\text{--}71^\circ\text{C}/2$  Torr.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.32 (bs, 9 H), 1.22 (bd,  $J = 7$  Hz, 9 H) and 1.68 (m, 3 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta -62.8$  (m). IR (neat): 3000, 2930, 1475, 1465, 1390, 1340, 1250, 1165, 1105, 1060, 1020, 975, 905, 845, 835, 795, 750,

700 and 635  $\text{cm}^{-1}$ . Molecular weight (benzene): Found: 502 calcd.: 468.5. (Found: C, 30.79; H, 4.58.  $\text{C}_{12}\text{H}_{21}\text{F}_9\text{O}_3\text{Si}_3$  calcd.: C, 30.76; H, 4.52%).

**15:** b.p. 102–105°C/2 Torr.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.27 (bs, 12 H), 1.19 (bd,  $J = 7$  Hz, 12 H) and 1.60 (m, 4 H).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -62.8 (m). IR (neat): 3000, 2920, 1475, 1465, 1415, 1395, 1340, 1255, 1165, 1085, 1020, 975, 905, 840, 795, 760, 700, 690 and 645  $\text{cm}^{-1}$ . Molecular weight (benzene): Found: 656 calcd.: 624.7. (Found: C, 31.00; H, 4.59.  $\text{C}_{16}\text{H}_{28}\text{F}_{12}\text{O}_4\text{Si}_4$  calcd.: C, 30.76; H, 4.52%).

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