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THE PREPARATION OF ORGANOSILYL- AND ORGANOGERMYL-SUBSTITUTED FERROCENES

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SUMMARY

Twenty-one organosilyl- and organogermyl-substituted ferrocenes, most of which contain the M–M (M = Si or Ge) groupings, have been prepared and their ^1H NMR spectra have been recorded. The preparations of some organic derivatives of silicon and germanium used in the synthesis are also described.

INTRODUCTION

Although many organosilicon-containing ferrocenes have been reported[1], little interest has been shown in ferrocenes having M–M (M = Si or Ge) groupings. In an earlier paper[2] we briefly described the preparation and acid cleavage of disilanyl-substituted ferrocenes. With a view to providing further insight into the mechanism of the cleavage and in connection with other studies, we have prepared some organosilyl- and organogermyl-substituted ferrocenes, most of which contain the M–M groupings. In this paper we describe their synthesis, characterization, and ^1H NMR data. Their chemical reactions will be reported in succeeding papers.

RESULTS AND DISCUSSION

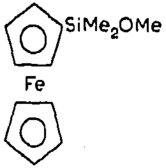
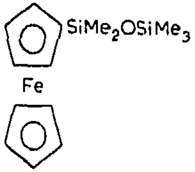
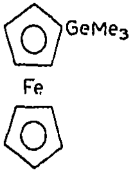
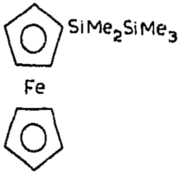
Structures, preparative methods, yields, and some physical properties for twenty-one ferrocenes prepared in this study are listed in Table 1, their analytical data in Table 2, and ^1H NMR data in Table 3.

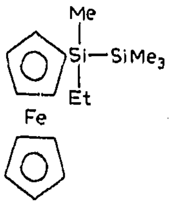
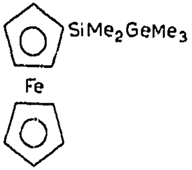
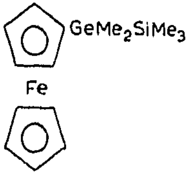
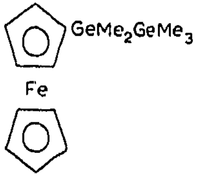
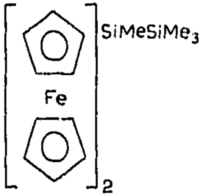
Compounds (I), (II), (III), (V), (XII), and (XX) are dark liquids, while compounds (IV), (VI), (VII), (VIII), (IX), (X), (XI), (XIII), (XIV), (XV), (XVI), (XVII), (XVIII), (XIX), and (XXI) are crystalline solids like ferrocene in appearance. In accordance with the statement by Rosenblum and Woodward[3] that ferrocene derivatives in which at least one ring remains unsubstituted exhibit absorptions in their IR spectra near 9 and 10 μ, compounds (I)–(X) do have the characteristic bands, while compounds (XI)–(XXI) do not. Most of the NMR peaks of the ferrocenes prepared can be definitely assigned. It is noticeable that the proton signals of the substituted cyclopentadienyl rings split into fairly clear $A'_2B'_2$ patterns and that bridged ferrocenes (XVII) and (XXI) do not exhibit the anomaly in the NMR spectra which is ascribed to ring tilting in the

(*continued on p.* 299)

TABLE 1

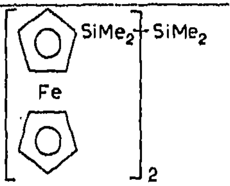
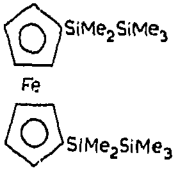
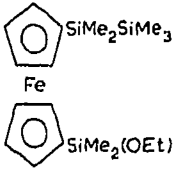
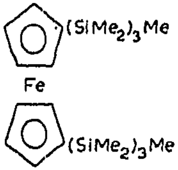
PREPARATION AND SOME PHYSICAL PROPERTIES OF ORGANOSILYL- AND ORGANOGERMYL-SUBSTITUTED FERROCENES

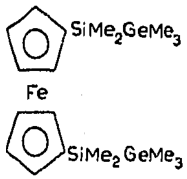
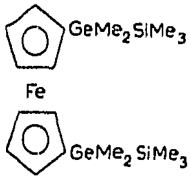
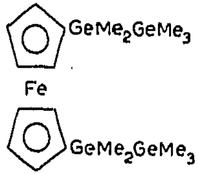
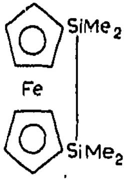
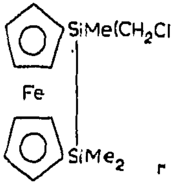
Compound			*Preparation*			*Properties*	
No.	*Name*	*Structure*	*Method*	*Silane or germane*	*Yield (%)*	*B.p. (°C/mm Hg) [m.p. (°C)]*	n_D^{20}
(I)	(Methoxydimethylsilyl)-ferrocene		A	$Me_2Si(OMe)_2$	5.4	102–105/2	1.5655
(II)	(Pentamethyldisiloxanyl)-ferrocene		A	$Me_3SiOSiMe_2Cl$	26.7	141/4	1.5280
(III)	(Trimethylgermyl)ferrocene		A	Me_3GeCl	12.2	115–116/3	1.5862
(IV)	(Pentamethyldisilanyl)-ferrocene		A	$Me_3SiSiMe_2Cl$	12.7	122–126/3	
						[59.0–60.0]	
			B	$Me_3SiSiMe_2Cl$	6.9		
			F	CpH + $CpMe_2SiSiMe_3$	12.6		

(V)	(α-Ethyltetramethyldisilanyl)ferrocene		B	$Me_3SiSiMeCl_2$	17.9	127/2
(VI)	[(Trimethylgermyl)dimethylsilyl]ferrocene		A	$Me_3GeSiMe_2Cl$	12.5	125–126/2 [43.0–44.0]
(VII)	[(Trimethylsilyl)dimethylgermyl]ferrocene		A	$Me_3SiGeMe_2Cl$	4.8	128–134/2 [56.0–57.0]
(VIII)	(Pentamethyldigermanyl)ferrocene		A	$Me_3GeGeMe_2Cl$	14.8	142–143/6 [43.4–43.8]
(IX)	1,1-Diferrocenyltetramethyldisilane		B	$Me_3SiSiMeCl_2$	17.8	[121–122]

(continued)

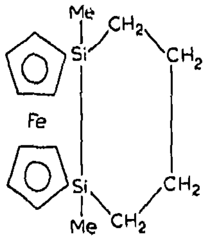
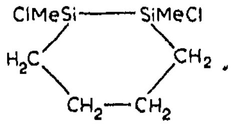
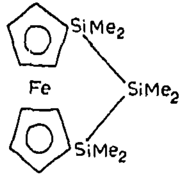
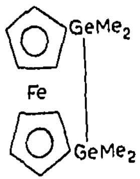
TABLE 1 (*continued*)

Compound			*Preparation*			*Properties*	
No.	*Name*	*Structure*	*Method*	*Silane or germane*	*Yield (%)*	*B.p. (°C/mm Hg) [m.p. (°C)]*	n_D^{20}
(X)	1,3-Diferrocenylhexamethyltrisilane[a]		C	$Cl(Me_2Si)_3Cl$	5.4	[136–137]	
(XI)	1,1′-Bis(pentamethyldisilanyl)ferrocene		D E F	$Me_3SiSiMe_2Cl$ $CpMe_2SiSiMe_3$ CpH + $CpMe_2SiSiMe_3$	57.2 54.7 35.5	[58.4]	
(XII)	1-(Ethoxydimethylsilyl)-1′-(pentamethyldisilanyl)-ferrocene		D	$Me_3SiSiMe_2Cl$ + $Me_2Si(OEt)_2$	[b]		1.5390
(XIII)	1,1′-Bis(heptamethyltrisilanyl)ferrocene[c]		E	$CpMe_2Si$-$(SiMe_2)_2Me$	37.7	[46.0–46.5]	

(XIV)	1,1′-Bis[(trimethylgermyl)dimethylsilyl]ferrocene		D	$Me_3GeSiMe_2Cl$	40.7	195–196/4 [45.0–46.0]
(XV)	1,1′-Bis[(trimethylsilyl)dimethylgermyl]ferrocene		D	$Me_3SiGeMe_2Cl$	78.8	163–174/2 [46.0–47.0]
(XVI)	1,1′-Bis(pentamethyldigermanyl)ferrocene		D	$Me_3GeGeMe_2Cl$	52.6	154–165/2 [36.0–37.0]
(XVII)	1,1′-(Tetramethyldisilanylene)ferrocene[d,e]		D E	$ClMe_2SiSiMe_2Cl$ $CpMe_2SiSiMe_2Cp$	34.3 [b]	[132–134]
(XVIII)	1,1′-[(Chloromethyl)trimethyldisilanylene]ferrocene		D	$Cl(ClCH_2)MeSi$- $-SiMe_2Cl$	20.0	130–145/0.03 [92.5–93.5]

(continued)

TABLE 1 (*continued*)

Compound			*Preparation*			*Properties*	
No.	*Name*	*Structure*	*Method*	*Silane or germane*	*Yield* (%)	*B.p.* (°C/*mm Hg*) [*m.p.* (°C)]	n_D^{20}
(XIX)	1,2-(1,1'-Ferrocenylene)-1,2-dimethyl-1,2-disila cyclohexane		D		22.5	161–165/0.16 [72.0–72.5]	
(XX)	1,1'-(Hexamethyltri-silanylene)ferrocene		C D	$Cl(Me_2Si)_3Cl$ $Cl(Me_2Si)_3Cl$	10.8 49.9	141–144/1	1.5920
(XXI)	1,1'-(Tetramethyldi-germanylene)ferrocene[e,f]		D	$ClMe_2GeGeMe_2Cl$	44.1	[138.5–139.5]	

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[a] Found: Mol.wt. cryoscopic in benzene, 544. $C_{26}H_{36}Fe_2Si_3$ calcd.: Mol.wt., 545. [b] Not determined. [c] Found: Mol.wt. cryoscopic in benzene, 560. $C_{24}H_{50}FeSi_6$ calcd.: Mol.wt., 563. [d] Found: Mol.wt. cryoscopic in benzene, 305; by mass spectroscopy, 300. $C_{14}H_{20}FeSi_2$ calcd.: Mol.wt., 300. [e] The X-ray study of these compounds is being carried out by Professor Shimada of the Osaka City University. [f] Molecular weight found (mass spectrometry) 389; $C_{14}H_{20}FeGe_2$ calcd. 389.

case of a carbon analog, 1,1,2,2-tetramethyl[2]ferrocenophane[4], presumably because the M–M (M = Si or Ge) bonds are longer than the C–C bond.

Most of these compounds were synthesized by treating chloro (or alkoxy)-silanes or chlorogermanes with lithiated ferrocenes. The monosubstituted derivatives were mainly prepared from "monolithioferrocene" obtained by the action of n-butyllithium on ferrocene in a mixed solvent of n-hexane/ether (1/1)[5] (Method A). Monolithioferrocene was also prepared from the reaction of (chloromercuri)ferrocene with ethyllithium in ether [6] (Method B). In earlier stages of this investigation, a mixture of mono- and dilithioferrocene resulting from metalation with n-butyllithium in ether/tetrahydrofuran (THF)[7] was frequently employed (Method C). In this paper, however, only the preparation of (X) and (XX) by this method is described, because other methods later proved to be better. Heteroannularly disubstituted derivatives were most conveniently prepared from the reaction of 1,1′-dilithioferrocene obtained by metalation with n-butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) complex in n-hexane[8] (Method D). In general, 1,1′-disubstituted ferrocenes could be prepared in satisfactory yields, whereas the monosubstituted compounds were obtained only in much lower yields.

TABLE 2

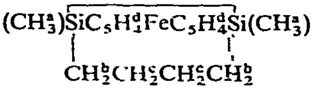
ANALYTICAL DATA FOR ORGANOSILYL- AND ORGANOGERMYL-SUBSTITUTED FERROCENES

Compound		*Analysis found (calcd.) (%)*			
No.	*Formula*	*C*		*H*	
(I)	$C_{13}H_{18}FeOSi$	57.59	(56.94)	6.91	(6.62)
(II)	$C_{15}H_{24}FeOSi_2$	54.36	(54.22)	7.42	(7.28)
(III)	$C_{13}H_{18}FeGe$	51.67	(51.58)	5.99	(5.99)
(IV)	$C_{15}H_{24}FeSi_2$	56.91	(56.95)	7.76	(7.65)
(V)	$C_{16}H_{26}FeSi_2$	58.56	(58.16)	7.99	(7.93)
(VI)	$C_{15}H_{24}FeGeSi$	50.08	(49.92)	7.00	(6.70)
(VII)	$C_{15}H_{24}FeGeSi$	50.05	(49.92)	6.99	(6.70)
(VIII)	$C_{15}H_{24}FeGe_2$	44.31	(44.44)	6.01	(5.97)
(IX)	$C_{24}H_{30}Fe_2Si_2$	59.14	(59.27)	6.13	(6.22)
(X)	$C_{26}H_{36}Fe_2Si_3$	57.32	(57.35)	6.73	(6.66)
(XI)	$C_{20}H_{38}FeSi_4$	53.97	(53.77)	8.55	(8.57)
(XII)	$C_{19}H_{34}FeOSi_3$	55.05	(54.52)	8.43	(8.19)
(XIII)	$C_{24}H_{50}FeSi_6$	51.30	(51.20)	9.04	(8.95)
(XIV)	$C_{20}H_{38}FeGe_2Si_2$	45.23	(44.84)	7.36	(7.15)
(XV)	$C_{20}H_{38}FeGe_2Si_2$	44.54	(44.84)	6.99	(7.15)
(XVI)	$C_{20}H_{38}FeGe_4$	39.03	(38.39)	6.52	(6.12)
(XVII)	$C_{14}H_{20}FeSi_2$	56.07	(55.99)	6.88	(6.71)
(XVIII)	$C_{14}H_{19}ClFeSi_2$	50.92	(50.23)	5.69	(5.72)
(XIX)	$C_{16}H_{22}FeSi_2$	58.92	(58.88)	7.02	(6.79)
(XX)	$C_{16}H_{26}FeSi_3$	53.70	(53.61)	7.33	(7.31)
(XXI)	$C_{14}H_{20}FeGe_2$	43.03	(43.19)	5.02	(5.18)

Some of the silyl-substituted ferrocenes were also synthesized by metalation with n-butyllithium in ether/THF of appropriately substituted cyclopentadienes either alone (Method E) or in an equimolar mixture with cylopentadiene itself (Method F), followed by treatment with ferrous chloride[9,10]:

TABLE 3

^1H NMR DATA FOR ORGANOSILYL- AND ORGANOGERMYL-SUBSTITUTED FERROCENES

Compound		*Chemical shifts (τ-values)*[a]					
No.	*Formula*	H_a	H_b	H_c	H_d	H_e	H_f
(I)	$C_5H_5^cFeC_5H_4^dSi(CH_3^a)_2OCH_3^b$	9.70 (s)	6.64 (s)	5.95 (s)	5.83 $(A'_2B'_2)$		
(II)	$C_5H_5^cFeC_5H_4^dSi(CH_3^b)_2OSi(CH_3^a)_3$	9.94 (s)	9.55 (s)	6.01 (s)	5.92 $(A'_2B'_2)$		
(III)	$C_5H_5^bFeC_5H_4^cGe(CH_3^a)_3$	9.66 (s)	6.00 (s)	5.95 $(A'_2B'_2)$			
(IV)	$C_5H_5^cFeC_5H_4^dSi(CH_3^b)_2Si(CH_3^a)_3$	9.97 (s)	9.71 (s)	5.96 (s)	5.93 $(A'_2B'_2)$		
(V)	$C_5H_5^dFeC_5H_4^eSi(CH_3^b)(CH_2^cCH_3^c)Si(CH_3^a)_3$	9.96 (s)	9.76 (s)	9.05 (m)	5.93 (s)	5.86 $(A'_2B'_2)$	
(VI)	$C_5H_5^cFeC_5H_4^dSi(CH_3^b)_2Ge(CH_3^a)_3$	9.86 (s)	9.64 (s)	5.96 (s)	5.91 $(A'_2B'_2)$		
(VII)	$C_5H_5^cFeC_5H_4^dGe(CH_3^b)_2Si(CH_3^a)_3$	9.86 (s)	9.64 (s)	5.96 (s)	5.95 $(A'_2B'_2)$		
(VIII)	$C_5H_5^cFeC_5H_4^dGe(CH_3^b)_2Ge(CH_3^a)_3$	9.76 (s)	9.58 (s)	5.97 (s)	5.95 $(A'_2B'_2)$		
(IX)	$(C_5H_5^cFeC_5H_4^d)_2Si(CH_3^b)Si(CH_3^a)_3$	9.83 (s)	9.45 (s)	5.98 (s)	5.87 $(A'_2B'_2)$		
(X)	$[C_5H_5^cFeC_5H_4^dSi(CH_3^b)_2]_2Si(CH_3^a)_2$	10.05 (s)	9.77 (s)	5.97 (s)	5.94 $(A'_2B'_2)$		
(XI)	$Fe[C_5H_4^cSi(CH_3^b)_2Si(CH_3^a)_3]_2$	9.98 (s)	9.71 (s)	5.91 $(A'_2B'_2)$			
(XII)	$(CH_3^a)_3SiSi(CH_3^b)_2C_5H_4^eFeC_5H_4^fSi(CH_3^b)_2OCH_2^dCH_3^c$	10.00 (s)	9.70 (bs)	8.88 (t)	6.41 (q)	5.91 $(A'_2B'_2)$	5.88 $(A'_2B'_2)$
(XIII)	$Fe[C_5H_4^dSi(CH_3^c)_2Si(CH_3^a)_2Si(CH_3^b)_3]_2$	10.02 (s)	10.00 (s)	9.64 (s)	5.76 $(A'_2B'_2)$		
(XIV)	$Fe[C_5H_4^cSi(CH_3^b)_2Ge(CH_3^a)_3]_2$	9.86 (s)	9.62 (s)	5.96 $(A'_2B'_2)$			
(XV)	$Fe[C_5H_4^cGe(CH_3^b)_2Si(CH_3^a)_3]_2$	9.86 (s)	9.61 (s)	6.00 $(A'_2B'_2)$			
(XVI)	$Fe[C_5H_4^cGe(CH_3^b)_2Ge(CH_3^a)_3]_2$	9.74 (s)	9.54 (s)	5.94 $(A'_2B'_2)$			
(XVII)	$(CH_3^a)_2\underline{SiC_5H_4^bFeC_5H_4^bSi}(CH_3^a)_2$	9.68 (s)	5.80 $(A'_2B'_2)$				
(XVIII)	$(CH_3^a)_2\underline{SiC_5H_4^cFeC_5H_4^cSi}(CH_2^bCl)(CH_3^a)$	9.67[b] (s) 9.56[b] (bs)	7.16[b] (s)	5.88[b] (m) 5.62[b] (m)			
(XIX)	 $\overline{(CH_3^a)SiC_5H_4^dFeC_5H_4^dSi}(CH_3^a)$ with $CH_2^bCH_2^cCH_2^cCH_2^b$	9.69 (s)	9.01 (m)	8.19 (m)	5.94 (m) 5.62 (m) 5.47 (m)		
(XX)	$(CH_3^a)_2\underline{SiC_5H_4^cFeC_5H_4^cSi(CH_3^a)_2Si}(CH_3^b)_2$	9.78 (s)	9.73 (s)	5.93 $(A'_2B'_2)$			
(XXI)	$(CH_3^a)_2\underline{GeC_5H_4^bFeC_5H_4^bGe}(CH_3^a)_2$	9.47 (s)	5.77 $(A'_2B'_2)$				

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[a] s, singlet; bs, broad singlet; t, triplet; q, quartet; m, multiplet. [b] Determined in benzene solution with cyclohexane as a internal standard.

$$\mathrm{CpMe_2SiSiMe_2Cp} \xrightarrow[\text{2. FeCl}_2]{\text{1. n-BuLi, ether/THF}} \mathrm{(XVII)}$$

$$\mathrm{CpH + CpMe_2SiSiMe_3} \xrightarrow[\text{2. FeCl}_2]{\text{1. n-BuLi, ether/THF}} \mathrm{(IV) + (XI) + Ferrocene}$$

(Cp = cyclopentadienyl group)

As briefly mentioned in an earlier paper[11], attempts to prepare compound (XX) from 1,3-dicyclopentadienylhexamethyltrisilane by Method (E) were unsuccessful, because metalation appeared not to proceed appreciably under the reaction conditions.

(Trimethylgermyl)dimethylchlorosilane, which was used as the chloride component for synthesis of (VI) and (XIV), was prepared by the sequence of reactions as shown below:

$$\mathrm{Me_3GeCl + PhMe_2SiLi} \xrightarrow{\text{THF}} \mathrm{Me_3GeSiMe_2Ph + LiCl}$$

$$\mathrm{Me_3GeSiMe_2Ph + HCl} \xrightarrow[\text{in CHCl}_3]{\text{AlCl}_3} \mathrm{Me_3GeSiMe_2Cl + PhH}$$

Similarly, (trimethylsilyl)dimethylchlorogermane used for synthesis of (VII) and (XV) was prepared as follows:

$$\mathrm{Me_3SiCl + PhMe_2GeLi} \xrightarrow{\text{THF}} \mathrm{Me_3SiGeMe_2Ph + LiCl}$$

$$\mathrm{Me_3SiGeMe_2Ph + HCl} \xrightarrow[\text{in CHCl}_3]{\text{AlCl}_3} \mathrm{Me_3SiGeMe_2Cl + PhH}$$

EXPERIMENTAL

All boiling and melting points are uncorrected. Reactions using organolithium compounds were carried out in an oxygen-free dry nitrogen atmosphere. IR spectra were recorded on a Hitachi EPI G3 grating spectrophotometer. NMR spectra were obtained on a Varian T60 spectrometer in carbon tetrachloride solution with cyclohexane as an internal standard and the data are given in τ-values. Molecular weights were obtained from mass spectra measured on a Hitachi RMS-4 mass spectrometer or by cryoscopic methods.

Starting materials

The silanes and germanes in the following list are known and were prepared by standard methods. The references given after the compounds are to the source or method of preparation: $\mathrm{Me_3SiOSiMe_2Cl}$ (ref. 12), $\mathrm{Me_3GeCl}$ (ref. 13), $\mathrm{Me_3SiSiMe_2Cl}$ (ref. 13), $\mathrm{CpMe_2SiSiMe_3}$ (ref. 2), $\mathrm{Me_3GeGeMe_2Cl}$ (refs. 14 and 15), $\mathrm{Cl(Me_2Si)_2Cl}$ (refs. 13, 16 and 17), $\mathrm{Cl(Me_2Si)_3Cl}$ (refs. 13, 17 and 18), $\mathrm{Cl(ClCH_2)MeSiSiMe_2Cl}$ (ref. 19), 1,2-dichloro-1,2-dimethyl-1,2-disilacyclohexane (ref. 20) and $\mathrm{ClMe_2GeGeMe_2Cl}$ (ref. 21). Several other silanes and germanes are new or have been mentioned only briefly as unpublished results in a review article[22]. Detailed procedures for their synthesis are given below.

1,1-*Dichlorotetramethyldisilane*, *$Me_3SiSiMeCl_2$*

(*a*). To ice-cooled concentrated sulfuric acid (150 g), 50 g (0.185 mol) of 1,1-diphenyltetramethyldisilane[23] was added dropwise with vigorous stirring during a period of 30 min. After stirring for an additional 15 min, 30 g (0.56 mol) of ammonium chloride was added in several portions at the same temperature. The resulting organic layer was separated and distilled under reduced pressure to give 21 g (61% yield) of 1,1-dichlorotetramethyldisilane, b.p. 146°, n_D^{20} 1.4530, d_4^{20} 1.0014. (Found: C, 25.82; H, 6.21; Cl, 37.63. $C_4H_{12}Cl_2Si_2$ calcd.: C, 25.66; H, 6.46; Cl, 37.87%.) NMR: 9.74 [s, $Si(CH_3)_3$] and 9.20 [s, $Si(CH_3)$].

(*b*). To a solution of 10.5 g (0.0388 mol) of 1,1-diphenyltetramethyldisilane[23] in 20 ml of benzene was added 0.5 g of freshly sublimed aluminum chloride. Dry hydrogen chloride was then passed through the mixture at room temperature for 1.5 h and a small amount of acetone was then added to deactivate the catalyst. The resulting mixture was flash-distilled under reduced pressure. Fractional distillation of the distillate gave 5 g (69% yield) of 1,1-dichlorotetramethyldisilane.

(*Trimethylgermyl*)*phenyldimethylsilane*, *$Me_3GeSiMe_2Ph$*

To a solution of 30 g (0.196 mol) of chlorotrimethylgermane in 50 ml of THF was added a solution of phenyldimethylsilyllithium, prepared from 33.4 g (0.196 mol) of phenyldimethylchlorosilane and 5.5 g (0.784 g-atom) of lithium in 100 ml of THF, with cooling in an ice bath over a 30-min period. The mixture was stirred at room temperature for 10 h and then hydrolyzed with cooling. The resulting organic layer was separated and the aqueous phase was extracted with ca. 100 ml of ether. The combined organic layer was worked up in the usual way. Fractional distillation gave 21.5 g (43.4% yield) of (trimethylgermyl)phenyldimethylsilane, b.p. 119–120°/26 mm Hg, n_D^{20} 1.5170. (Found: C, 52.51; H, 8.25. $C_{11}H_{20}GeSi$ calcd.: C, 52.23; H, 7.97%.) NMR: 9.86 (s, $GeCH_3$), 9.63 (s, $SiCH_3$), and 2.74 (m, C_6H_5).

(*Trimethylsilyl*)*phenyldimethylgermane*, *$Me_3SiGeMe_2Ph$*

To a solution of 19 g (0.172 mol) of trimethylchlorosilane in 50 ml of THF, a solution of phenyldimethylgermyllithium, prepared from 37 g (0.172 mol) of phenyldimethylchlorogermane and 4.8 g (0.684 g-atom) of lithium in 100 ml of THF, was added with cooling in an ice-bath during a period of 30 min. The mixture was stirred at room temperature for 10 h and then hydrolyzed with cooling. The resulting organic layer was separated and the aqueous phase was extracted with ca. 100 ml of ether. The organic layer was fractionally distilled to give 22 g (73.5% yield) of (trimethylsilyl)-phenyldimethylgermane, b.p. 94–98°/5 mm Hg, n_D^{20} 1.5181, d_4^{20} 1.0502. (Found: C, 52.82; H, 8.26. $C_{11}H_{20}GeSi$ calcd.: C, 52.23; H, 7.97%.) NMR: 9.88 (s, $SiCH_3$), 9.63 (s, $GeCH_3$), and 2.80 (m, C_6H_5).

(*Trimethylgermyl*)*dimethylchlorosilane*, *$Me_3GeSiMe_2Cl$*

In a 100 ml three-necked flask, equipped with a gas inlet tube, a stirrer and a reflux condenser, was placed a mixture of 19 g (75 mmol) of $Me_3GeSiMe_2Ph$, 50 ml of chloroform and 0.3 g (2.24 mmol) of aluminum chloride. Dry hydrogen chloride was passed into the mixture with stirring at room temperature, a slightly exothermic reaction occurred. The extent of reaction was monitored by GLC analysis (Apiezon L 30% on Celite, 260°) of aliquots periodically extracted from the reaction mixture. After about 3 h, the starting material had disappeared, with formation of a single product indicated to be homogeneous by GLC. At this point the introduction of hydrogen chloride was discontinued and ca. 10 ml of acetone was added. Removal by distillation of the solvent and benzene produced during the reaction, followed by fractional distillation of the residue gave 3.3 g (20.9% yield) of (trimethylgermyl)dimethylchlorosilane, b.p. 143–144°, n_D^{20} 1.4560. (Found: C, 28.13; H, 7.24. $C_5H_{15}ClGeSi$ calcd.: C, 28.42; H, 7.16%.) NMR: 9.76 (s, $GeCH_3$) and 9.49 (s, $SiCH_3$).

(Trimethylsilyl)dimethylchlorogermane, $Me_3SiGeMe_2Cl$

Similarly, a mixture of 32 g (0.126 mol) of $Me_3SiGeMe_2Ph$, 200 ml of chloroform and 1.0 g (7.44 mmol) of aluminum chloride was treated with dry hydrogen chloride. After work-up as above, there was obtained 17 g (63.9% yield) of (trimethylsilyl)dimethylchlorogermane, b.p. 77–80°/42 mm Hg, n_D^{20} 1.4710. (Found: C, 28.29; H, 7.31. $C_5H_{15}ClGeSi$ calcd.: C, 28.42; H, 7.16%.) NMR: 9.72 (s, $SiCH_3$) and 9.33 (s, $GeCH_3$).

Cyclopentadienylheptamethyltrisilane, $CpMe_2Si(SiMe_2)_2Me$

Cyclopentadienylmagnesium bromide was prepared in the usual way by treatment of 20 g (0.303 mol) of cyclopentadiene with ethylmagnesium bromide (0.226 mol) in 200 ml of an ether/benzene (1/1) mixture over a 5-h period. To this reagent was added in 5 min 40 g (0.178 mol) of chloroheptamethyltrisilane and the mixture was heated at reflux for 12 h. The mixture was then hydrolyzed and the resulting organic layer was worked up in the usual way. Fractional distillation gave 21 g (46.3% yield) of cyclopentadienylheptamethyltrisilane, b.p. 80°/25 mm Hg, n_D^{20} 1.5126, d_4^{20} 0.8681, MR_D 88.09 (calcd. 88.15). (Found: C, 57.55; H, 10.57. $C_{12}H_{26}Si_3$ calcd.: C, 56.61; H, 10.29%.)

1,2-Dicyclopentadienyltetramethyldisilane, $CpMe_2SiSiMe_2Cp$

Cyclopentadienylmagnesium bromide was prepared from 0.654 mol of ethylmagnesium bromide in 300 ml of an ether/benzene (1/1) mixture and 55 g (0.832 mol) of cyclopentadiene over a 5-h period. To this reagent 53 g (0.283 mol) of 1,2-dichlorotetramethyldisilane was added during 20 min, and the mixture was then heated under gentle reflux for 13 h. After work-up, fractional distillation gave 30 g (43.1% yield) of 1,2-dicyclopentadienyltetramethyldisilane, b.p. 102°/2.4 mm Hg, n_D^{20} 1.5422, d_4^{20} 0.9604, MR_D 80.80 (calcd.: 82.22). (Found: C, 68.10; H, 9.34. $C_{14}H_{22}Si_2$ calcd.: C, 68.22; H, 9.00%.)

Methods of preparation of substituted ferrocenes

Method (A). The following detailed description of the synthesis of compound (IV) is typical of Method (A).

Ferrocene (30 g, 0.162 mol) in 450 ml of ether was metalated with 0.168 mol of n-butyllithium in 200 ml of n-hexane at room temperature over an 8-h period. To this solution was added gradually 29.2 g (0.175 mol) of chloropentamethyldisilane, and the mixture was then heated under gentle reflux for 4 h. It was hydrolyzed and the resulting organic layer was separated. Evaporation of the solvent resulted in precipitation of unchanged ferrocene which was removed by filtration. Fractional distillation of the filtrate gave 6.5 g of (IV). A pure sample was obtained by fractional sublimation and recrystallization from petroleum ether.

Method (*B*). This method is exemplified by the syntheses of (IX) and (V). To a solution of 32 g (0.076 mol) of (chloromercuri)ferrocene in 450 ml of ether, 0.172 mol of ethyllithium in 210 ml of ether was added with cooling in an ice-bath over a 15-min period, and the mixture was stirred at room temperature for 2 h. To this mixture 8 g (0.043 mol) of 1,1-dichlorotetramethyldisilane was then added during 5 min, and the mixture was stirred at room temperature for 76 h and subsequently refluxed for 24 h. Most of the solvent and diethylmercury was distilled off and the residue was extracted first with petroleum ether and then with benzene in a Soxhlet apparatus. Removal of solvents from the combined extracts left crystals. Recrystallization from petroleum ether gave 3.3 g of (IX). Distillation of the mother liquid from the recrystallization gave 5 g of (V).

Method (*C*). This method is essentially the same as Method (A) except that the metalation of ferrocene was carried out by treatment of its THF solution with n-butyllithium in ether.

Method (*D*). This method is also substantially the same as Method (A) except that the ferrocene was metalated by treatment of its n-hexane solution with a mixture of n-butyllithium in n-hexane and ca. 0.8 equivalent of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine.

Method (*E*). The synthesis of compound (XIII) is typical of this method. To a solution of 18 g (0.071 mol) of 1-cyclopentadienylheptamethyltrisilane in 100 ml of THF, 0.078 mol of n-butyllithium in 120 ml of ether was added at $-20°$ over a 10-min period, and the mixture was then stirred for 2 h. To this mixture at $-20°$ was added during 10 min, ferrous chloride prepared from 4.3 g (0.026 mol) of anhydrous ferric chloride and 0.7 g (0.013 g-atom) of iron powder in 100 ml of THF. The mixture was stirred for 1 h and allowed to stand overnight. It was then heated at reflux for 5 h. Most of the solvent was removed by distillation and the residue was extracted with petroleum ether in a Soxhlet apparatus. The crystalline residue resulting from the extracts after evaporation of the solvent was recrystallized from petroleum ether to give 8.3 g of (XIII).

Method (*F*). To a mixture of 39.3 g (0.2 mol) of cyclopentadienylpentamethyldisilane and 14 g (0.2 mol) of cyclopentadiene in 70 ml of THF was added 0.4 mole of n-butyllithium in 200 ml of ether at $-15°$. Subsequent procedures were essentially the same as described under Method (E). Fractional sublimation and recrystallization of the residue left after evaporation of the solvent from the extract gave 8.0 g of (IV), 8.0 g of (XI), and 6.6 g (35.5% yield) of ferrocene.

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