Journal of Organometallic Chemistry, 430 (1992) 273–286
Elsevier Sequoia S.A., Lausanne
JOM 22513

Organometalloidal derivatives of the transition metals

XXX*. Mass spectrometry of transition metal substituted disilanes

Antonio Guerrero, Jacobo Gómez-Lara, Jorge Cervantes
Facultad de Quimica, Universidad de Guanajuato, Guanajuato, 36050 (Mexico)

Luis Velasco
Instituto de Quimica, Universidad Autonoma de Mexico, Cuidad Universitaria, DF 04510 (Mexico)

Hemant Sharma and Keith H. Pannell
Department of Chemistry, The University of Texas at El Paso, El Paso, TX 79968 (USA)

(Received August 21, 1991)

Abstract

Mass spectral fragmentation of a series of transition metal substituted disilanes, $LMSiMe_2SiMe_2ML$, $LM = (\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}$ (Fp), $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{-}$ (Fc), $RFe(CO)_2(\eta^5\text{-}C_5H_4)$, are reported. They exhibit significant distinctions depending on the nature of LM. Direct cleavage of the Si–Si bond occurs in the order Fc ≫ Fp ≫ $RFe(CO)_2(\eta^5\text{-}C_5H_4)$ owing to the capacity of the LM fragment to stabilize positive charge. For complexes containing a direct Fe–Si bond, *i.e.* $Fp\text{–}SiMe_2SiMe_2ML$, disilene complexed ions are observed, and those complexes containing both an Fp group and a $(\eta^5\text{-}C_5H_4\text{–}SiMe_2SiMe_2)$ group exhibit significant formation of $(C_5H_4{=}Si{=}SiMe_2)$ complexed ions. Little disproportionation is observed for any of the complexes studied, in contrast to organodisilanes.

Introduction

The recent upsurge in interest in the chemical and physical properties of poly- and oligosilanes stems from their potential as photoresists, preceramics, and photoconducting materials, etc. [2–6]. In our laboratories we are interested in the synthesis and study of both oligo- and polysilanes with transition metal substituents, since the metal imparts special characteristics unavailable with traditional organic substituents. The transition metal substituent $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{–}$

Correspondence to: Dr. K.H. Pannell, Department of Chemistry, The University of Texas at El Paso, TX 79968, USA.

* For Part XXIX, see ref. 1.

(Fp), has been shown to induce a unique series of rearrangements, isomerizations and de-oligomerizations in oligosilanes, *e.g.* eqs. 1–3 [7–10].

$$\mathrm{Fp{-}SiMe_2SiMe_2SiMe_2SiMe_3 \xrightarrow{h\nu} Fp{-}Si(SiMe_3)_3} \qquad (1)$$

$$\mathrm{IFp{-}SiMe_2SiMe_2Ph \xrightarrow[IFp\,=\,(\eta^5\text{-indenyl})Fe(CO)_2]{h\nu} IFp{-}SiMePhSiMe_3} \qquad (2)$$

$$\begin{tikzcd}
\mathrm{Fp{-}SiMe_2SiMe_2{-}Fp} \arrow[r, "h\nu"] & \mathrm{(\eta^5\text{-}C_5H_5)Fe(CO)_2(\mu\text{-}CO)(\mu\text{-}MeSiSiMe_3)} \arrow[d, "h\nu"] & (3a) \\
& \mathrm{[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}SiMe_2)_2} & (3b)
\end{tikzcd}$$

The Fp substituent has the capacity to lengthen Si–Si bonds in the α position with respect to the metal. Thus, the complex Fp–$SiMe_2SiMe_2$–Fp possesses a Si–Si bond of 2.390 Å, significantly longer than normal for organodisilanes, while the Si–Si bond in $CH_3Fe(CO)_2[\eta^5\text{-}C_5H_4SiMe_2SiMe_2(\eta^5\text{-}C_5H_4)Fe(CO)_2Me]$ in which similar types of Fp groups are bonded to the tetramethyldisilane via the cyclopentadienyl ligands, is in the normal range of Si–Si bond lengths (2.341 Å) [11]. Even those complexes of disilanes that possess only a single Fp type of substituent exhibit an elongated Si–Si bond [12]. On the other hand, ferrocenyl substituents, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$ (Fc) do not create any Si–Si bond lengthening and provide no activation of the Si–Si bond with respect to photochemistry, indeed they have a significant stabilizing effect [13*,14].

As part of our general investigation into the nature of the Si–Si bond in transition metal substituted oligosilanes we have initiated a mass spectroscopic analysis of such complexes. An aim of this study is to see if the chemical, photochemical and structural features noted above may be observed from the different fragmentation patterns obtained from the appropriate oligosilanes. We wish to report a study on the fragmentation patterns observed for a series of bis-1,2-organometallo-1,1,2,2-tetramethyldisilanes, using both Fp and Fc type substituents, *i.e.* LM–$Me_2SiSiMe_2$–ML, LM = Fp; Fc; $(\eta^5\text{-}C_5H_4)Fe(CO)_2R$, R = Me.

Experimental

The various metal substituted disilanes were synthesized using published procedures [10,11]. Mass spectra were obtained using a Hewlett–Packard HP-5985B with 70 eV electron beam, via direct inlet into the ionization chamber maintained at 125°C. We obtained and analyzed the mass spectra of $FcSiMe_2SiMe_2Fc$ (I), $FcSiMe_2SiMe_2Fp$ (II), $FpSiMe_2SiMe_2Fp$ (III), $MeFe(CO)_2\{\eta^5\text{-}C_5H_4SiMe_2SiMe_2\text{-}Fe(CO)_2(\eta^5\text{-}C_5H_5)\}$ (IV), and $\{MeFe(CO)_2(\eta^5\text{-}C_5H_4)\}_2SiMe_2SiMe_2$ (V). The various ions observed, their relative abundances and percentage of ion current carried, *i*, and their proposed formulations, are recorded in Tables 1–5. Competing fragmentation pathways often gave rise to complex envelopes of ions. We therefore used computed simulations to provide the data recorded in the tables for such regions. An example of such simulations is illustrated in Fig. 1 for the ions 17, 18, and 19 observed in the spectrum of complex V. The overall possibile fragmenta-

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* Reference with asterisk indicates a note in the list of references.

Table 1

Fragmentation scheme of compound $H_{30}C_{24}Fe_2Si_2$ (I)

	% RA	m/e	Condensed formula	Fragment	i
1	35	486	$H_{30}C_{24}Fe_2Si_2$	$Cp_2Fe_2(\eta^5\text{-}Me_2SiC_5H_4)_2$ +	12.1
2	100	243	$H_{15}C_{12}FeSi$	$CpFe(\eta^5\text{-}Me_2SiC_5H_4)^+$	34.6
3	10	213	$H_9C_{10}FeSi$	$CpFe(\eta^5\text{-}SiC_5H_4)^+$	3.46
4	2	186	$H_{10}C_{10}Fe$	$CpFeCp^+$	0.86
5	2	163	H_7C_6FeSi	$Fe(\eta^5\text{-}MeSiC_5H_4)^+$	0.86
6	5	148	H_4C_5FeSi	$Fe(\eta^5\text{-}SiC_5H_4)^+$	1.73
7	25	121	H_5C_5Fe	$Fe(\eta^5\text{-}C_5H_5)^+$	8.67
8	18	107	H_7C_6Si	$(C_5H_4)SiMe^+$	6.07
9	35	93	H_5C_5Si	$CpSi^+$	12.1
10	12	73	H_9C_3Si	Me_3Si^+	4.16
11	20	56	Fe	Fe^+	7.8
12	8	43	H_3CSi	$MeSi^+$	2.6

tions associated with the disilanes are illustrated in Scheme 1, while detailed fragmentation patterns for I and III are presented in Scheme 2a (I) and Scheme 2b (III) and they are available from the authors as supplementary material for the remainder of the complexes. The various structures proposed are based upon best estimates based upon known chemistry of the systems studied.

Discussion

There are several published reports concerning the mass spectral fragmentation patterns of disilanes [15–26]. The conclusions from these studies suggests that four major fragmentation pathways may be expected:

(a) Simple cleavage of the Si–Si bond.
(b) Loss of organic radicals, and/or elimination of organic species.
(c) Cleavage of the Si–Si bond with concurrent disproportionation, and/or molecular rearrangement.
(d) Cleavage of the Si–Si bond with concurrent silene formation.

The most intriguing of the above fragmentation routes is the disproportionation reaction. Along with the ubiquitous cleavage of the Si–Si bonds, Chambers and Glockling [15] and Gaidis *et al.* [17] established that the molecular ion in disilanes, *i.e.* $[R_3Si\text{–}SiR'_3]^+$, could readily form a doubly bridged ion $[R_2Si(\mu\text{-}R)(\mu\text{-}R')SiR'_2]^+$ leading to formation of both $[R_2R'Si]^+$ and $[R'_2RSi]^+$ upon Si–Si bond cleavage. In the event that R and R′ were non-equivalent the relative amounts of bridging by the two groups suggested a random process. Such 1,2-migrations have been reported for Me, Ph, OMe, and vinyl groups [15,16,24,25]. Elimination of formaldehyde from methoxy disilanes [16,19,24,21] and ethylene from ethyldisilanes [15], typify elimination of organic molecules resulting in the formation of $[R_nSiH]^+$ ions. Closely related to our interest are the studies by the Sakurai group [24] and Donyagina *et al.* [23] on permethylated oligosilanes in which elimination of the trimethylsilyl group, and successive dimethylsilylene units is routinely observed, plus the 4-membered transition state elimination to yield silene and

Table 2

Fragmentation scheme of compound $H_{26}C_{21}O_2Fe_2Si_2$ (II)

	% RA	m / e	Condensed formula	Fragment	i
1	38	478	$H_{26}C_{21}O_2Fe_2Si_2$	$CpFe(\eta^5\text{-}CpFe(CO)_2Me_4Si_2C_5H_4)^+$	5.74
2	<1	450	$H_{26}C_{20}O_1Fe_2Si_2$	$CpFe(\eta^5\text{-}CpFe(CO)Me_4Si_2C_5H_4)^+$	0.15
3	4	422	$H_{26}C_{19}FeSi_2$	$CpFe(\eta^5\text{-}CpFeMe_4Si_2C_5H_4)^+$	0.604
4	12	418	$H_{14}C_{17}O_2Fe_2Si_2$	$CpFe(\eta^5\text{-}CpFeSi_2C_5H_4)^+$	1.81
5	32	301	$H_{21}C_{14}Fe_1Si_2$	$CpFe(\eta^5\text{-}Me_4Si_2C_5H_4)^+$	4.83
6	43	299	$H_{15}C_{13}O_1Fe_1Si_2$	$(\eta^2\text{-}Si_2Me_2C_5H_4)Fe(CO)Cp^+$	6.5
7	8	285	$H_{13}C_{12}O_1Fe_1Si_2$	$(\eta^2\text{-}Si_2Me(H)C_5H_4)Fe(CO)Cp^+$	1.2
8	5	265	$H_{17}C_{10}O_1Fe_1Si_2$	$CpFe(CO)Si_2Me_4^+$	0.75
9	98	243	$H_{15}C_{12}Fe_1Si_1$	$CpFe(\eta^5\text{-}Me_2SiC_5H_4)^+$	14.8
10	18	242	$H_{10}C_{10}Fe_1Si_2$	$Cp_2FeSi_2^+$	2.72
11	6	241	$H_9C_{10}Fe_1Si_2$	$CpFe(\eta^5\text{-}Si_2C_5H_4)^+$	0.91
12	13	235	$H_{11}C_9O_2Fe_1Si_1$	$CpFe(CO)_2SiMe_2^+$	1.96
13	10	228	$H_{12}C_{11}Fe_1Si_1$	$CpFe(\eta^5\text{-}MeSiC_5H_4)^+$	1.51
14	18	213	$H_9C_{10}Fe_1Si_1$	$CpFe(\eta^5\text{-}SiC_5H_4)^+$	2.72
15	10	207	$H_{11}C_8O_1Fe_1Si_1$	$CpFe(CO)SiMe_2^+$	1.51
16	8	186	$H_{10}C_{10}Fe_1$	$CpFeCp^+$	1.20
17	23	179	$H_{11}C_7Fe_1Si_1$	$CpFeSiMe_2^+$	3.47
18	8	177	$H_5C_7O_2Fe_1$	$CpFe(CO)_2^+$	1.20
19	5	163	$H_7C_6Fe_1Si_1$	$Fe(\eta^5\text{-}MeSiC_5H_4)^+$	0.76
20	5	151	$H_{11}C_7Si_2$	$CpSi_2Me_2^+$	0.91
21	15	149	$H_5C_5Fe_1Si_1$	$CpFeSi^+$	2.26
22	7	148	$H_4C_5Fe_1Si_1$	$Fe(\eta^5\text{-}SiC_5H_4)^+$	1.05
23	4	123	$H_{11}C_7Si_1$	$CpSiMe_2^+$	0.61
24	100	121	H_5C_5Fe	$CpFe^+$	15.1
25	12	107	$H_7C_6Si_1$	$MeSiC_5H_4^+$	1.96
26	5	98	$H_2C_1Fe_1Si_1$	$FeSiCH_2^+$	0.76
27	11	95	$H_3C_3Fe_1$	$FeC_3H_3^+$	1.66
28	2	94	$H_2C_3Fe_1$	$FeC_3H_2^+$	0.31
29	19	93	$H_5C_5Si_1$	$CpSi^+$	2.87
30	15	86	$H_6C_2Si_2$	$MeSiSiMe^+$	2.2
31	23	73	$H_9C_3Si_1$	$SiMe_3^+$	3.47
32	23	56	Fe	Fe^+	3.47
33	5	43	$H_3C_1Si_1$	$MeSi^+$	0.76
34	5	39	H_3C_3	$(CH\text{–}CH\text{–}CH)^+$	0.76

disilene cationic species. Finally it has been suggested that vinyldisilanes undergo a complex rearrangement to form silaindene upon electron impact [25].

For some of the transition metal disilane complexes under investigation, we expect further fragmentation pathways involving stepwise loss of CO ligands, due to the presence of transition metal carbonyl groups. All of the above general patterns of fragmentation are observed to a greater or lesser extent, however, there are important distinctions between the various complexes showing that the disilane is very susceptible to the nature of the metal substituents.

$FcSiMe_2SiMe_2Fc$ (I) (Table 1)

Ferrocene has long been recognized as an important group in the stabilization of positive charge on the α-atom of the cyclopentadienyl ligand [27]. Therefore, as noted from the data in Table 1 the major fragmentation for bis-1,2-ferrocenyl-1,1,2,2,-tetramethyldisilane, $FcSiMe_2SiMe_2Fc$ (I) is the simple cleavage of the

Table 3

Fragmentation scheme of compound $H_{22}C_{18}O_4Fe_2Si_2$ (III)

	% RA	*m/e*	Condensed formula	Fragment	*i*
1	5	470	$H_{22}C_{18}O_4Fe_2Si_2$	$Cp_2Fe_2(CO)_4Me_4Si_2^+$	0.46
2	5	427	$H_{19}C_{16}O_3Fe_2Si_2$	$Cp_2Fe_2(CO)_3Me_3Si_2^+$	0.15
3	3	397	$H_{13}C_{14}O_4Fe_2Si_2$	$Cp_2Fe_2(CO)_3Me_1Si_2^+$	0.308
4	8	386	$H_{22}C_{15}O_1Fe_2Si_2$	$Cp_2Fe_2(CO)_1Me_4Si_2^+$	0.46
5	25	358	$H_{22}C_{14}Fe_2Si_2$	$Cp_2Fe_2Me_4Si_2^+$	0.71
6	13	356	$H_{16}C_{13}O_1Fe_2Si_2$	$Cp_2Fe_2(CO)_1Me_2Si_2^+$	0.61
7	43	354	$H_{10}C_{12}O_2Fe_2Si_2$	$Cp_2Fe_2(CO)_2Si_2^+$	0.71
8	8	352	$H_8C_{12}O_2Fe_2Si_2$	$(CO)_1FeC_5H_4Si_2C_5H_4Fe(CO)_1^+$	0.46
9	10	342	$H_{18}C_{13}Fe_2Si_2$	$CpFei\eta^5\text{-}Me_3Si_2(C_5H_4)iFe^+$	0.15
10	8	341	$H_{17}C_{13}Fe_2Si_2$	$Me_3Si_2(\eta^5\text{-}C_5H_4)_2Fe_2^+$	0.15
11	8	340	$H_{12}C_{12}O_1Fe_2Si_2$	$CpFe(CO)(\eta^5\text{-}Me_2Si_2C_5H_4)Fe^+$	0.15
12	4	326	$H_{14}C_{12}Fe_2Si_2$	$Me_2Si_2(\eta^5\text{-}C_5H_4)_2Fe_2^+$	0.15
13	2	312	$H_{12}C_{11}Fe_2Si_2$	$CpFe(\eta^5\text{-}Me_2Si_2C_5H_4)Fe^+$	0.46
14	4	298	$H_{10}C_{10}Fe_2Si_2$	$Cp_2Fe_2Si_2^+$	0.77
15	8	296	$H_8C_{10}Fe_2Si_2$	$Fe_2(\eta^5\text{-}SiC_5H_4)_2^+$	2.77
16	75	293	$H_{17}C_{11}O_2Fe_1Si_2$	$(\eta^2\text{-}Me_4Si_2)Fe(\eta^5\text{-}(CO)_2Cp)^+$	11.55
17	100	265	$H_{17}C_{10}O_1Fe_1Si_2$	$(\eta^2\text{-}Me_4Si_2)Fe(\eta^5\text{-}(CO)_1Cp)^+$	15.5
18	20	237	$H_{17}C_9Fe_1Si_2$	$(\eta^2\text{-}Me_4Si_2)Fe(\eta^5\text{-}Cp)^+$	3.08
19	53	235	$H_{11}C_9O_2Fe_1Si_1$	$CpFe(CO)_2Me_2Si^+$	7.7
20	13	233	$H_5C_7O_2Fe_1Si_2$	$(\eta^2\text{-}Si_2)Fe(CO)_2(\eta^5\text{-}Cp)^+$	2.15
21	13	220	$H_8C_8O_2Fe_1Si_1$	$CpFe(CO)(SiMe)^+$	0.46
22	13	207	$H_{11}C_8O_1Fe_1Si_1$	$CpFe(CO)SiMe_2^+$	1.54
23	3	205	$H_5C_7O_2Fe_1Si_1$	$CpFe(CO)_2Si^+$	0.46
	3	205	$H_5C_6O_1Fe_1Si_1$	$(\eta^2\text{-}Si_2)Fe(CO)Cp^+$	0.46
24	18	186	$H_{10}C_{10}Fe$	Cp_2Fe^+	2.77
25	23	179	$H_{11}C_7Fe_1Si_1$	$CpFeSiMe_2^+$	3.85
26	8	177	$H_5C_7O_2Fe_1$	$CpFe(CO)_2^+$	0.77
	8	177	$H_5C_6O_1Fe_1Si_1$	$CpFe(CO)Si^+$	0.77
	8	177	$H_5C_5Fe_1Si_2$	$(\eta^2\text{-}Si_2)Fe(\eta^5\text{-}Cp)$	0.77
27	5	164	$H_8C_6Fe_1Si_1$	$CpFeSiMe^+$	0.77
28	8	149	$H_5C_5Fe_1Si_1$	$CpFeSi^+$	1.23
29	10	123	$H_{11}C_7Si$	$CpSiMe_2^+$	1.54
30	75	121	H_5C_5Fe	$CpFe^+$	11.55
31	10	98	H_2CFeSi	$FeSiCH_2^+$	2.0
32	10	95	H_3C_3Fe	$FeC_3H_3^+$	2.31
33	3	94	H_2C_3Fe	$FeC_3H_2^+$	1.23
34	27	93	H_5C_5Si	$CpSi^+$	7.7
35	5	84	FeSi	$FeSi^+$	1.54
36	18	73	H_9C_3Si	$SiMe_3^+$	2.7
37	33	56	Fe	Fe^+	5.08
38	4	43	$H_3C_1Si_1$	$SiMe^+$	0.61

Si–Si bond in the molecular ion ($m/e = 486$ [35%]) to produce the base ion $[FcSiMe_2]^+$. The only other ions of significance in the spectra of I are those typically associated with cyclopentadienyl iron complexes, $m/e = 121$, $[C_5H_5Fe]^+$; 56, Fe^+, along with ions associated with methylsilanes, *e.g.* $m/e = 43$, $[MeSi]^+$. There are two other ions of significance, $m/e = 93$, $[C_5H_5Si]^+$, and $m/e = 107$, $[C_5H_4SiMe]^+$ which occur throughout the various spectra. This ion has been observed previously by Aylett [28] and Malisch [29] and is thought to be a pyramidal $Si(\eta^5\text{-}C_5H_5)$ structure, of the type recently isolated by Jutzi and cowork-

Table 4

Fragmentation scheme of compound $H_{24}C_{19}O_4Fe_2Si_2$ (IV)

	% RA	*m/e*	Condensed formula	Fragment	*i*
1	8	484	$H_{24}C_{19}O_4Fe_2Si_2$	$Fp(\eta^5\text{-}Si_2Me_4C_5H_4)Fe(CO)_2Me^+$	0.55
2	3	456	$H_{24}C_{18}O_3Fe_2Si_2$	$Fp(\eta^5\text{-}Si_2Me_4C_5H_4)Fe(CO)_1Me^+$	0.21
3	20	428	$H_{24}C_{17}O_2Fe_2Si_2$	$Fp(\eta^5\text{-}Si_2Me_4C_5H_4)FeMe^+$	1.37
4	3	413	$H_{21}C_{16}O_2Fe_2Si_2$	$Fp(\eta^5\text{-}Si_2Me_3C_5H_4)FeMe^+$	0.21
5	45	400	$H_{24}C_{16}O_1Fe_2Si_2$	$CpFeCO(\eta^5\text{-}Si_2Me_4C_5H_4)FeMe^+$	3.09
6	13	398	$H_{18}C_{15}O_2Fe_2Si_2$	$Fp(\eta^5\text{-}Si_2Me_2C_5H_4)FeMe^+$	0.89
7	10	385	$H_{21}C_{15}O_1Fe_2Si_2$	$CpFeCO(\eta^5\text{-}Si_2Me_3C_5H_4)FeMe^+$	0.68
8	8	383	$H_{15}C_{14}O_2Fe_2Si_2$	$Fp(\eta^5\text{-}Si_2Me_1C_5H_4)FeMe^+$	0.55
9	70	372	$H_{24}C_{15}Fe_2Si_2$	$CpFe(\eta^5\text{-}Si_2Me_4C_5H_4)FeMe^+$	4.8
10	75	370	$H_{18}C_{14}O_1Fe_2Si_2$	$CpFeCO(\eta^5\text{-}Si_2Me_2C_5H_4]FeMe^+$	5.15
11	33	368	$H_{12}C_{13}O_2Fe_2Si_2$	$Fp(\eta^5\text{-}MeSi_2C_5H_4)FeMe^+$	2.27
12	43	357	$H_{21}C_{14}Fe_2Si_2$	$CpFe(\eta^5\text{-}Me_3Si_2C_5H_4)FeMe^+$	2.95
13	55	355	$H_{15}C_{13}O_1Fe_2Si_2$	$CpFeCO(\eta^5\text{-}MeSi_2C_5H_4)FeMe^+$	3.78
14	15	353	$H_9C_{12}O_2Fe_1Si_2$	$Fp(\eta^5\text{-}Si_2C_5H_4)FeMe^+$	1.03
15	8	342	$H_{18}C_{13}Fe_2Si_2$	$CpFe(\eta^5\text{-}Me_2Si_2C_5H_4)FeMe^+$	0.55
16	8	340	$H_{12}C_{12}O_1Fe_2Si_2$	$CpFeCO(\eta^5\text{-}MeSi_2C_5H_4)Fe^+$	0.55
17	30	329	$H_{21}C_{14}Fe_2Si_1$	$CpFeMe(\eta^5\text{-}SiMe_2C_5H_4)FeMe^+$	2.06
18	10	314	$H_{18}C_{13}Fe_2Si_1$	$CpFe(\eta^5\text{-}SiMe_2C_5H_4)FeMe^+$	0.69
	10	314	$H_{18}C_{14}O_1Fe_1Si_2$	$(\eta^2\text{-}C_5H_4Me_2Si_2)FeCOMeCp^+$	0.69
19		312	$H_{12}C_{11}Fe_2Si_2$	$CpFe(\eta^5\text{-}Si_2MeC_5H_4)Fe^+$	0.55
20	6	307	$H_{20}C_{12}O_2Fe_1Si_2$	$FeMe(CO)_2(\eta^5\text{-}Me_4Si_2C_5H_4)^+$	0.69
21	15	299	$H_{15}C_{12}Fe_2Si_1$	$CpFe(\eta^5\text{-}SiMe_2C_5H_4)Fe^+$	1.03
	15	299	$H_{15}C_{13}O_1Fe_1Si_2$	$(\eta^5\text{-}C_5H_4Me_2Si_2)FeCOCp^+$	1.03
22	17	298	$H_{10}C_{10}Fe_2Si_2$	CpFeSiSiFeCp	1.16
23	8	297	$H_9C_{10}Fe_2Si_2$	$CpFe(\eta^5\text{-}Si_2C_5H_4)Fe^+$	0.55
24	33	293	$H_{17}C_{11}O_2Fe_1Si_2$	$[\eta^2\text{-}Me_4Si_2]Fe[\eta^5\text{-}(CO)_2Cp]^+$	2.27
25	84	265	$H_{17}C_{10}O_1Fe_1Si_2$	$[\eta^2\text{-}Me_4Si_2]Fe[\eta^5\text{-}(CO)Cp]^+$	5.77
26	18	249	$H_{13}C_{10}O_2Fe_1Si_1$	$(\eta^5\text{-}Me_2SiC_5H_4)Fe(CO)_2Me^+$	1.23
27	15	237	$H_{17}C_9Fe_1Si_2$	$[\eta^2\text{-}(Me_4Si_2)]Fe[\eta^5\text{-}Cp]^+$	1.03
28	78	235	$H_{11}C_9O_2Fe_1Si_1$	$CpFe(CO)_2Me_2Si^+$	5.36
29	15	233	$H_5C_7O_2Fe_1Si_2$	$[\eta^2\text{-}Si_2]Fe(CO)_2[\eta^5\text{-}Cp]^+$	1.03
30	13	219	$H_7C_8O_2Fe_1Si_1$	$(\eta^5\text{-}SiC_5H_4)Fe(CO)_2Me^+$	0.89
31	23	207	$H_{11}C_8O_1Fe_1Si_1$	$CpFe(CO)SiMe_2^+$	1.58
32	5	205	$H_5C_7O_2Fe_1Si_1$	$CpFe(CO)_2Si^+$	0.34
	5	205	$H_5C_6O_1Fe_1Si_1$	$(\eta^2\text{-}Si_2)Fe(CO)Cp^+$	0.34
33	13	193	$H_{13}C_8Fe_1Si_1$	$C_5H_4FeMeSiMe_2^+$	0.89
34	5	191	$H_7C_8O_2Fe_1$	$(\eta^5\text{-}C_5H_4)Fe(CO)_2Me^+$	0.34
35	18	186	$H_{10}C_{10}Fe$	Cp_2Fe^+	1.23
36	18	179	$H_{11}C_7Fe_1Si_1$	$CpFeSiMe_2^+$	2.6
37	15	177	$H_5C_7O_2Fe_1$	$CpFe(CO)_2^+$	1.03
	15	177	$H_5C_6O_1Fe_1Si_1$	$CpFe(CO)Si^+$	1.03
	15	177	$H_5C_5Fe_1Si_2$	$(\eta^2\text{-}Si_2)Fe(\eta^5\text{-}Cp)^+$	1.03
38	8	164	$H_8C_6Fe_1Si_1$	$CpFeSiMe^+$	0.55
39	10	163	$H_7C_6Fe_1Si_1$	$(\eta^5\text{-}C_5H_4)FeSiMe^+$	0.69
40	13	149	$H_5C_5Fe_1Si_1$	$CpFeSi^+$	0.89
41	15	148	$H_4C_5Fe_1Si_1$	$(\eta^5\text{-}C_5H_4)FeSi^+$	1.03
42	13	123	$H_{11}C_7Si_1$	$CpSiMe_2^+$	0.89
43	100	121	$H_5C_5Fe_1$	$CpFe^+$	1.03
44	15	107	$H_7C_6Si_1$	$(C_5H_4)SiMe^+$	1.03
45	13	98	$H_2C_1Fe_1Si_1$	$FeSiCH_2^+$	0.89
46	15	95	$H_3C_3Fe_1$	$FeC_3H_3^+$	1.03
47	7	94	$H_2C_3Fe_1$	$FeC_3H_2^+$	0.48
48	43	93	$H_5C_5Si_1$	$CpSi^+$	2.9

Table 4 (continued)

	% RA	m/e	Condensed formula	Fragment	i
49	5	84	Fe_1Si_1	$FeSi^+$	0.34
50	18	73	$H_9C_3Si_1$	$SiMe_3^+$	1.23
51	10	71	$H_3C_1Fe_1$	$FeMe^+$	0.69
52	25	56	Fe	Fe^+	1.71
53	3	43	$H_3C_1Si_1$	$SiMe^+$	0.21

ers, and supported by theoretical calculations [30,31]. We observed no evidence for disproportionation during Si–Si bond cleavage involving appearance of either Fc_2Si or Me_3SiFc species, although very minor ions of $[Me_3Si]^+$ could be observed, $m/e = 73$ (12% abundance at 3.2 retention time; *cf.* only 2% abundance at 5.7 s).

$FcSiMe_2SiMe_2Fp$ (II) (Table 2)

A combination of the two metal substituents Fc and Fp in $FpSiMe_2SiMe_2Fc$ (II), changes the above pattern of fragmentation. Simple cleavage of the Si–Si bond is still observed in the molecular ion ($m/e = 478$ [38%]) and the ion $[FcSiMe_2]^+$ is present in 98% abundance, based upon the 100% abundance of $m/e = 121$, $[C_5H_5Fe]^+$. However, the other half of the molecular ion, *i.e.* $[FpSiMe_2]^+$, m/e 235, is only a minor ion [13%]. This observation reinforces the understanding that Fc stabilizes positive charge; upon fragmentation of $[FpSiMe_2SiMe_2Fc]^+$ little charge remains in the form of the $[FpSiMe_2]^+$ unit. This latter ion loses the two CO groups to form a minor ion at $m/e = 179$ (23%), $[C_5H_5FeSiMe_2]^+$. Significant ions are observed at $m/e = 418$ [12%] corresponding to the complete stripping of methyl groups from the two silicon atoms in the molecular ion, and at m/e 450, 422 resulting in the loss of 1 and 2 CO groups from the molecular ion. Apart from the expected ions mentioned above in conjunction with I. *i.e.* $m/e = 121$, 107, 93, and 43, the spectrum of II exhibits major ions at $m/e = 299$ [43%] and 301 [32%]. The ion at $m/e = 301$ is readily explained by cleavage of the Si–Fe bond in the parent to produce $[FcSiMe_2SiMe_2]^+$. The ion at $m/e = 299$ will be discussed below in terms of its formation from complexes IV and V since it is only formed from complexes that contain both an $(\eta^5\text{-}C_5H_4)SiMe_2SiMe_2$ grouping and an Fp group.

$FpSiMe_2SiMe_2Fp$ (III) (Table 3)

Two Fp substituents on the disilane create a totally new type of fragmentation. A small molecular ion is observed, $m/e = 470$ [5%], but by far the largest ions present in the spectrum are those at $m/e = 293$ [75%], (A) and 265 [100%] (B). These are well understood in terms of the initial loss of an Fp unit from the molecular ion to form $[FpSi_2Me_4]^+$ (A), followed by loss of a CO group, representing ions of a disilene complexed to the Fe atom. Complexes of the type $[Fp(olefin)]^+$ have long been well characterized [32] and recently several examples of disilene complexes have been reported [33], thus the formation of such ions is to be expected during the fragmentation process. A significant amount of symmetrical Si–Si bond cleavage is also observed to produce the ion $m/e = 235$ [53%]. As expected, ions at $m/e = 121$ [75%], 93 [27%], and 73 [18%] are exhibited showing

Table 5

Fragmentation scheme of compound $H_{26}C_{20}O_4Fe_2Si_2$ (V)

	% RA	m/e	Condensed formula	Fragment	i
1		498	$H_{26}C_{20}O_4Fe_2Si_2$	$Si_2Me_4(\eta^5\text{-}C_5H_4)_2Fe_2(CO)_4Me_2^+$	–
2	12	470	$H_{26}C_{19}O_3Fe_2Si_2$	$Si_2Me_4(\eta^5\text{-}C_5H_4)_2Fe_2(CO)_3Me_2^+$	0.84
3	2	455	$H_{23}C_{18}O_3Fe_2Si_2$	$Si_2Me_3(\eta^5\text{-}C_5H_4)_2Fe_2(CO)_3Me_2^+$	0.14
4	4	442	$H_{26}C_{18}O_2Fe_2Si_2$	$Si_2Me_4(\eta^5\text{-}C_5H_4)_2Fe_2(CO)_2Me_2^+$	0.28
5	6	427	$H_{23}C_{17}O_2Fe_2Si_2$	$Si_2Me_3(\eta^5\text{-}C_5H_4)_2Fe_2(CO)_2Me_2^+$	0.42
6	9	414	$H_{26}C_{17}O_1Fe_2Si_2$	$Si_2Me_4(\eta^5\text{-}C_5H_4)_2Fe_2(CO)Me_2^+$	0.63
7	29	412	$H_{20}C_{16}O_2Fe_2Si_2$	$Si_2Me_2(\eta^5\text{-}C_5H_4)_2Fe_2(CO)_2Me_2^+$	2.03
8	4	410	$H_{14}C_{15}O_3Fe_2Si_2$	$Si_2(\eta^5\text{-}C_5H_4)_2Fe_2(CO)_3Me_2$	0.28
9	12	399	$H_{23}C_{16}O_1Fe_2Si_2$	$Si_2Me_3(\eta^5\text{-}C_5H_4)_2Fe_2(CO)Me_2^+$	0.84
10	20	398	$H_{18}C_{15}O_2Fe_2Si_2$	$CpFe(CO)_2Si_2Me_2(\eta^5\text{-}C_5H_4)FeMe^+$	1.40
11	28	386	$H_{26}C_{16}Fe_2Si_2$	$Si_2Me_4(\eta^5\text{-}C_5H_4)_2Fe_2Me_2^+$	1.96
12	14	384	$H_{20}C_{15}O_1Fe_2Si_2$	$Si_2Me_2(\eta^5\text{-}C_5H_4)_2Fe_2(CO)Me_2^+$	0.98
13	8	382	$H_{14}C_{14}O_2Fe_2Si_2$	$Si_2(\eta^5\text{-}C_5H_4)_2Fe_2(CO)_2Me_2^+$	0.56
14	62	371	$H_{23}C_{15}Fe_2Si_2$	$Si_2Me_3(\eta^5\text{-}C_5H_4)_2Fe_2Me_2^+$	4.34
15	62	370	$H_{18}C_{14}O_1Fe_2Si_2$	$CpFe(CO)Si_2Me_2(\eta^5\text{-}C_5H_4)FeMe^+$	4.34
16	33	369	$H_{17}C_{14}O_1Fe_2Si_2$	$Si_2Me(\eta^5\text{-}C_5H_4)_2Fe_2(CO)Me_2^+$	2.31
17	27	356	$H_{20}C_{14}Fe_2Si_2$	$Si_2Me_2(\eta^5\text{-}C_5H_4)_2Fe_2Me_2^+$	1.89
18	75	354	$H_{14}C_{13}O_1Fe_2Si_2$	$Me_2Si_2(\eta^5\text{-}C_5H_4)_2Fe_2(CO)^+$	5.25
19	14	352	$H_8C_{12}O_2Fe_2Si_2$	$Fe_2(CO)_2(\eta^5\text{-}C_5H_4)_2Si_2^+$	0.98
20	3	343	$H_{23}C_{16}O_1Fe_1Si_2$	$FeMeCO(\eta^5\text{-}C_5H_4(Me_4Si_2C_5H_4))^+$	0.21
21	8	340	$H_{12}C_{12}O_1Fe_2Si_2$	$CpFe(CO)(\eta^5\text{-}MeSi_2C_5H_4)Fe^+$	0.56
22	10	330	$H_{22}C_{15}O_1Fe_1Si_1$	$CpFeMe(CO)Si_2Me(\eta^5\text{-}C_5H_5)^+$	0.70
23	4	328	$H_{20}C_{15}O_1Fe_1Si_1$	$FeMe(CO)(\eta^5\text{-}C_5H_4Si_2Me_3C_5H_4)^+$	0.28
24	15	314	$H_{18}C_{13}Fe_2Si_1$	$CpFe(\eta^5\text{-}SiMe_2C_5H_4)FeMe^+$	1.05
25	15	314	$H_{18}C_{14}O_1Fe_1Si_2$	$(\eta^5\text{-}C_5H_4Me_2Si_2)Fe(CO)MeCp^+$	1.05
26	20	313	$H_{15}C_{12}O_1Fe_1Si_1$	$FeMe(CO)(\eta^5\text{-}C_5H_4Si_2Me_2C_5H_4)^+$	1.40
27	17	312	$H_{12}C_{11}Fe_2Si_2$	$CpFe(\eta^5\text{-}Si_2MeC_5H_4)Fe^+$	1.19
28	73	300	$H_{20}C_{14}Fe_1Si_2$	$Fe(\eta^5\text{-}C_5H_4Si_2Me_4C_5H_4)^+$	5.11
29	100	299	$H_{15}C_{12}Fe_2Si_1$	$CpFe(SiMe_2C_5H_4)^+$	7.00
	100	299	$H_{15}C_{13}O_1Fe_1Si_2$	$(\eta^2\text{-}C_5H_4Me_2Si_2)Fe(CO)Cp^+$	7.00
30	22	298	$H_{10}C_{10}Fe_2Si_2$	$CpFeSiSiFeCp^+$	1.54
31	22	298	$H_{14}C_{12}Fe_2Si$	$SiMe_2(\eta^5\text{-}C_5H_4)_2Fe_2^+$	1.54
32	21	297	$H_9C_{10}Fe_2Si_2$	$CpFe(\eta^5\text{-}Si_2C_5H_4)Fe^+$	1.47
33	2	293	$H_{17}C_{11}O_2Fe_1Si_2$	$(\eta^2\text{-}Me_4Si_2)Fe(\eta^5\text{-}(CO)_2Cp)^+$	0.14
34	26	285	$H_{17}C_{13}Fe_1Si_2$	$FeMe(\eta^5\text{-}C_5H_4Si_2Me_2C_5H_4)^+$	1.82
35	33	283	$H_{11}C_{11}Fe_2Si$	$SiMe_1(\eta^5\text{-}C_5H_4)_2Fe_2^+$	2.31
36	34	282	$H_6C_5O_3Fe_2Si_2$	$Fe(CO)Si_2Me_2Fe(CO)_2^+$	2.38
37	10	269	$H_9C_{11}O_1Fe_1Si_2$	$(\eta^2\text{-}C_5H_4Si_2)Fe(CO)Cp^+$	0.70
38	12	268	$H_8C_{10}Fe_2Si$	$Si(\eta^5\text{-}C_5H_4)_2Fe_2^+$	0.84
39	20	257	$H_{17}C_{13}Fe_1Si_1$	$FeMe(\eta^5\text{-}C_5H_4Si_1Me_2C_5H_4)^+$	1.40
40	13	256	$H_{12}C_{11}Fe_1Si_2$	$(\eta^2\text{-}C_5H_4Me_1Si_2)FeCp^+$	0.91
41	7	249	$H_{13}C_{10}O_2Fe_1Si_1$	$(\eta^5\text{-}Me_2SiC_5H_4)Fe(CO)_2Me^+$	0.49
42	28	243	$H_{16}C_{12}Fe_1S_1$	$CpFeSiMe_2C_5H_4^+$	1.96
43	29	242	$H_{14}C_{12}Fe_1Si_1$	$Fe(\eta^5\text{-}C_5H_4SiMe_2C_5H_4)^+$	2.03
44	18	241	$H_9C_{10}Fe_1Si_2$	$(\eta^2\text{-}C_5H_4Si_2)FeCp^+$	1.26
45	2	235	$H_{11}C_9O_1Fe_1Si_2$	$(\eta^2\text{-}Me_2Si_2)Fe(CO)Cp^+$	0.14
46	6	233	$H_5C_7O_2Fe_1Si_2$	$(\eta^2\text{-}Si_2)Fe(CO)_2Cp^+$	0.42
47	9	227	$H_{12}C_{11}Fe_1Si_1$	$Fe(\eta^5\text{-}C_5H_4SiMe_1C_5H_4)$	0.63
48	4	219	$H_7C_8O_2Fe_1Si_1$	$(\eta^5\text{-}SiC_5H_4)Fe(CO)_2Me^+$	0.28
49	2	207	$H_{11}C_7Fe_1Si_2$	$(\eta^2\text{-}Si_2Me_2)FeCp^+$	0.14
	2	207	$H_{11}C_8O_1Fe_1Si_1$	$CpFe(CO)SiMe_2^+$	0.14
50	7	205	$H_5C_7O_2Fe_1Si_1$	$CpFe(CO)_2Si^+$	0.49
	7	205	$H_5C_6O_1Fe_1Si_1$	$(\eta^2\text{-}Si_2)Fe(CO)Cp^+$	0.49
51	20	193	$H_{13}C_8Fe_1Si_1$	$C_5H_4FeMeSiMe_2^+$	1.40

Table 5 (continued)

	% RA	m/e	Condensed formula	Fragment	i
52	10	191	$H_7C_8O_2Fe_1$	$(\eta^5\text{-}C_5H_4)Fe(CO)_2Me^+$	0.70
53	2	186	$H_{10}C_{10}Fe$	Cp_2Fe^+	0.14
54	7	179	$H_{11}C_7Fe_1Si_1$	$CpFeSiMe_2^+$	0.49
55	18	178	$H_{10}C_7Fe_1Si_1$	$(\eta^5\text{-}C_5H_4)FeSiMe_2^+$	1.26
56	8	177	$H_5C_7O_2Fe_1$	$CpFe(CO)_2^+$	0.56
	8	177	$H_5C_6O_1Fe_1Si_1$	$CpFe(CO)Si^+$	0.56
	8	177	$H_5C_5Fe_1Si_2$	$(\eta^2\text{-}Si_2)Fe(\eta^5\text{-}Cp)$	0.56
57	6	164	$H_8C_6Fe_1Si_1$	$CpFeSiMe^+$	0.42
58	16	163	$H_7C_6Fe_1Si_1$	$(\eta^5\text{-}C_5H_4)FeSiMe^+$	1.12
59	9	149	$H_5C_5Fe_1Si_1$	$CpFeSi^+$	0.63
60	26	148	$H_4C_5Fe_1Si_1$	$(\eta^5\text{-}C_5H_4)FeSi^+$	1.82
61	14	135	$H_7C_6Fe_1$	$(\eta^5\text{-}C_5H_4)FeMe^+$	0.98
	14	135	$H_7C_6Si_2$	$(C_5H_4)Si_2Me^+$	0.98
62	8	123	$H_{11}C_7Si_1$	$CpSiMe_2^+$	0.56
63	57	121	$H_5C_5Fe_1$	$CpFe^+$	3.99
64	30	107	$H_7C_6Si_1$	$(C_5H_4)SiMe^+$	2.10
65	5	99	$H_3C_1Fe_1Si_1$	$FeSiMe^+$	0.35
66	11	98	$H_2C_1Fe_1Si_1$	$FeSiCH_2^+$	0.77
67	9	95	$H_3C_3Fe_1$	$FeC_3H_3^+$	0.63
68	8	94	$H_2C_3Fe_1$	$FeC_3H_2^+$	0.56
69	50	93	$H_5C_5Si_1$	$CpSi^+$	3.50
70	16	84	Fe_1Si_1	$FeSi^+$	1.12
71	8	81	$H_1C_2Fe_1$	$FeC_2H_1^+$	0.56
72	42	73	$H_9C_3Si_1$	$SiMe_3^+$	2.94
73	32	71	$H_3C_1Fe_1$	$FeMe^+$	2.24
74	31	56	Fe	Fe^+	2.17
75	9	43	$H_3C_1Si_1$	$SiMe^+$	0.63

again, in the case of the latter ion, the ability for some disproportionation of the Si–Si bond, *i.e.* formation of $[Me_3Si]^+$.

$FpSiMe_2SiMe_2\text{-}\{(\eta^5\text{-}C_5H_4)Fe(CO)_2Me\}$ *(IV) (Table 4)*

A small molecular ion is observed, $m/e = 484$ (8%), followed by successive loss of the four CO groups, ions at $m/e = 456$ [3%], 428 [20%], 400 [45%], 372 [70%]. The major fragmentation observed for this complex involves the rupture of the Si–Si bond to form a major ion at $m/e = 235$ [78%], $[(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2]^+$, with a smaller ion resulting from the other half of the molecular ion at $m/e = 249$ [18%], $[(\eta^5\text{-}C_5H_4SiMe_2)Fe(CO)_2Me]^+$. As with complex III, major fragmentation of the molecular ions results in the formation of the disilene iron species A, $[Fp(Me_2Si{=}SiMe_2)]^+$, $m/e = 293$ [33%], and $[A\text{–}CO]^+$, $m/e = 265$ [84%]. The ions at $m/e = 299$ and 285 noted for II are again observed (see below).

$((\eta^5\text{-}C_5H_4)Fe(CO)_2Me)_2(SiMe_2SiMe_2)$ *(V) (Table 5)*

There is no molecular ion observed and very limited direct cleavage of the Si–Si bonds observed in the spectra. The fragmentation pattern following the formation of the highest observable m/e ion is competitive loss of the CO and Me groups noted above. Major envelopes of ions are observed in the regions $m/e = 299$ and 285, common to complexes II and IV. It is only possible to speculate upon the nature of these ions observed for the complexes containing both the Fp system and a (η^5-$C_5H_4SiMe_2SiMe_2$) group. Our best estimate for the structural assignment for the ion $m/e = 299$ represents a complexed, conjugated, disila-allene, $[(C_5H_4{=}Si{=}SiMe_2)(\eta^5\text{-}C_5H_5)Fe(CO)]^+$, but we have no experimental evidence to back up this suggestion. Ions due to further fragmentation of this species are also observed for all the complexes II, IV, and V.

Conclusions

Some overall conclusions may be drawn from the present study with respect to the initial fragmentation of the disilanes (Scheme 1).

(a) As noted from the data summarized in Table 6, direct cleavage of the Si–Si bond is not observed equally for all the metal complexes. In the case of the bis-ferrocenyl complex (I), the majority of the ion current is in the form of ions derived by such direct cleavage and a significant amount of direct cleavage also occurs for $FcSi_2Me_4Fp$. In both cases the ability of the Fc unit to stabilize positive charge renders such cleavage favourable, such that the $[FpSiMe_2]^+$ ion represent only 2% of the total ion current for complex II (*cf.* $[FcSiMe_2]^+ = 15\%$). When both ends of the disilane are bonded to Fp units, III, this changes; the $[FpSiMe_2]^+$ ion increases in significance for total ion current, but not to the extent observed for the ferrocene substituent in I and II. Complexes in which the silicon atoms are

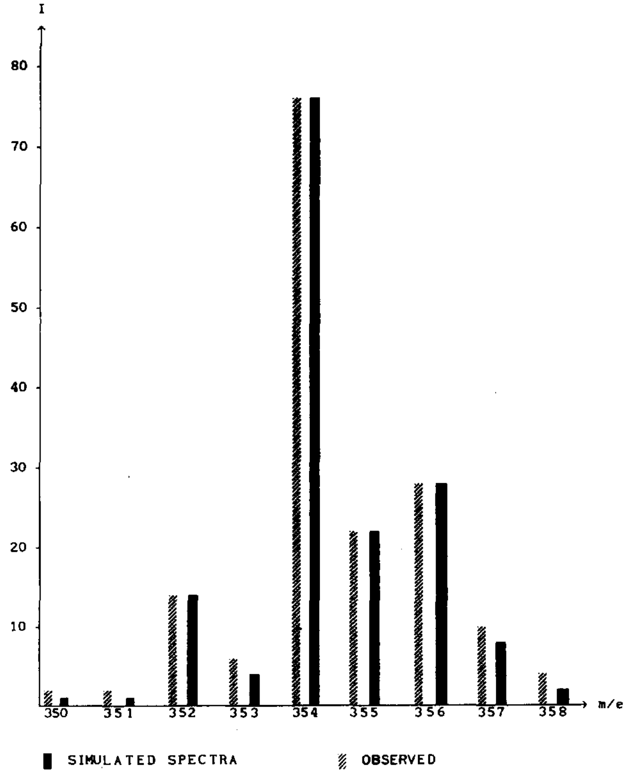
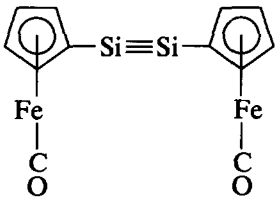
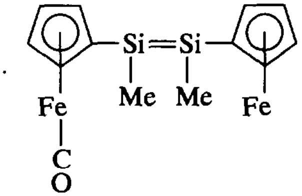


Fig. 1. (a) Observed and simulated spectra for fragments 17, 18, and 19 in complex V, $C_{26}H_{20}O_4Fe_2Si_2$.

Fragment 19 $H_8C_{12}O_2Fe_2Si_2$ ($m/e = 352$)



Fragment 18 $H_{14}C_{13}O_1Fe_2Si_2$ ($m/e = 354$)



Fragment 17 $H_{20}C_{14}Fe_2Si_2$ ($m/e = 356$)

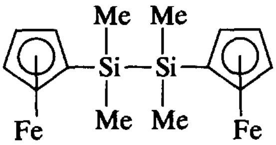
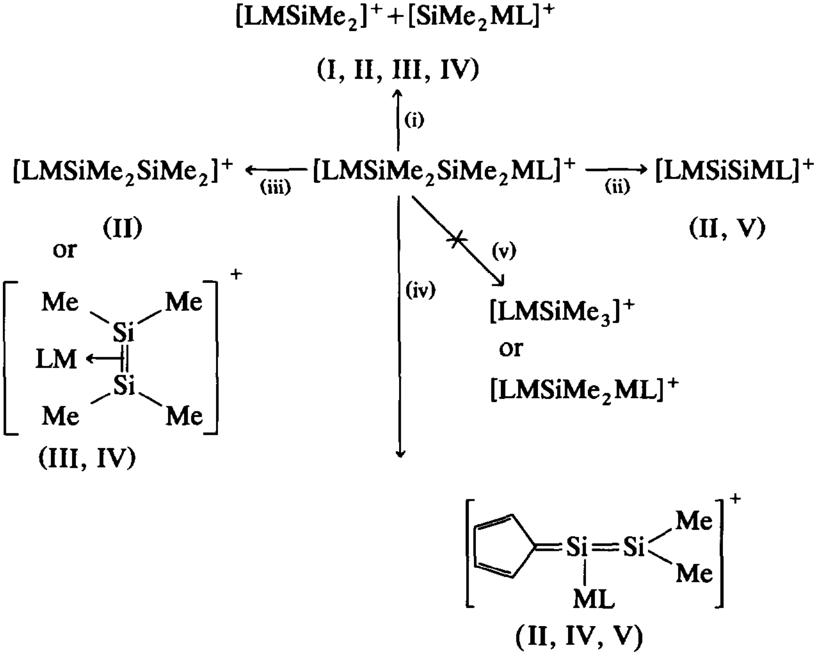
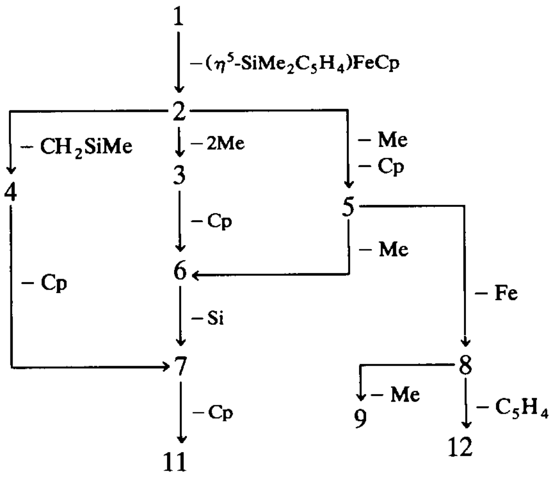


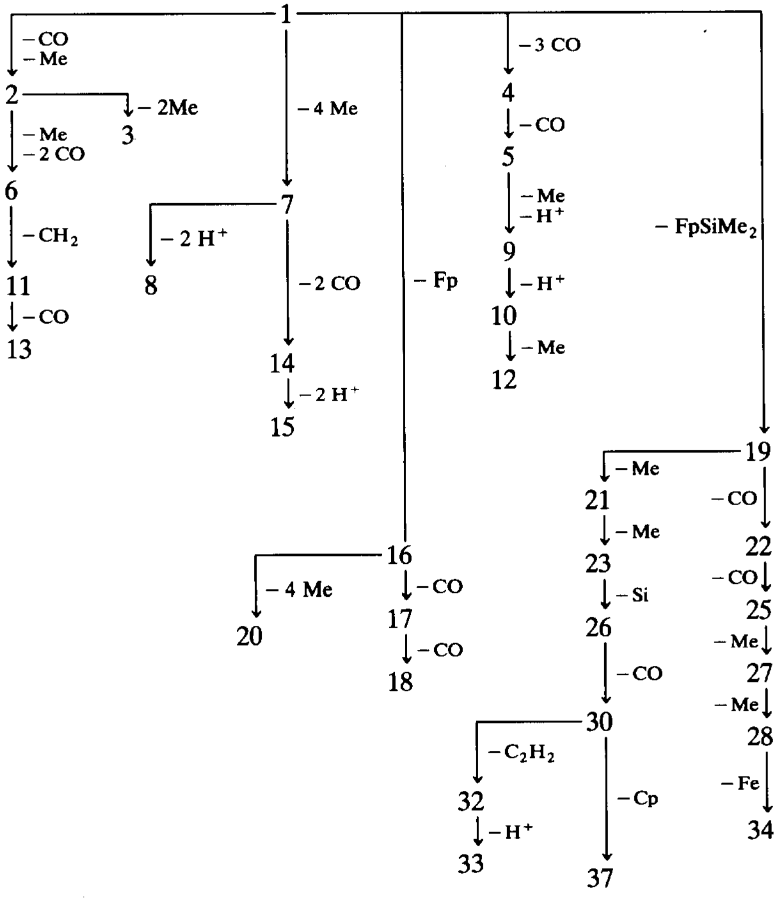
Fig. 1. (b) Proposed structures for fragments 17, 18, and 19 in complex V.



Scheme 1. Possible fragmentation pathways of transition-metal substituted disilanes (LM = Fp, (η^5-C_5H_4)Fe(CO)$_2$R, R = Me; Fc). (i) Symmetrical cleavage of Si–Si bond; (ii) loss of methyl groups to form silylyne complex; (iii) cleavage of Fe–Si bond to form disilene complex; (iv) stripping of methyl and carbonyl groups to form disila-allene complex; (v) cleavage of Si–Si bond with disproportionation.



Scheme 2. (a) Fragmentation scheme of compound $H_{30}C_{24}Fe_2Si_2$ (I).



Scheme 2. (b) Fragmentation scheme of compound $H_{22}C_{18}O_4Fe_2Si_2$ (III).

Table 6

Fragments abundance (%) for cleavage of Si–Si bond in compounds I–IV

Compound		$(L_nM)^+$	$(SiMe_2SiMe_2\text{-}M'L)^+$	$(L_nMSiMe_2)^+$	$(SiMe_2\text{-}M'L_n)^+$	$(L_nMSiMe_2\text{-}SiMe_2)^+$	$(M'L_n)^+$
I	L_nM = Fc $M'L_n$ = Fc	–	–	35	35	–	–
II	L_nM = Fc $M'L_n$ = Fp	–	–	15	2	5	1
III	L_nM = Fp $M'L_n$ = Fp	14	14	7	7	14	14
IV	L_nM = [a] $M'L_n$ = Fp	–	3	1	5	0.5	–

[a] $(\eta^5\text{-}C_5H_4)Fe(CO)_2Me$.

bonded to $(\eta^5\text{-}C_5H_4)Fe(CO)_2R$ groups exhibit almost no direct Si–Si cleavage. Thus we can order the various metal substituents L_nM in their capacity to support Si–Si bond cleavage as $Fc \gg Fp \gg (\eta^5\text{-}C_5H_4)Fe(CO)_2R$, resulting from their capacity to stabilize positive charge.

Thus in terms of fragmentation of the various disilanes, the Si–Si bond is therefore significantly less prone to rupture in III, IV, and V (*cf.* I and II). In the case of III and IV this is due to the favourable formation of disilene complex ions $[Fp(Me_2Si{=}SiMe_2)]^+$ while in the case of V (as well as II and IV) the stability of the ion *m/e* 299 plays an important role.

(b) Little or no disproportionation is observed, with the notable exception that significant amounts of $[Me_3Si]^+$ are observed. In no case could we assign a mother ion to this daughter fragment.

Conclusions (a) and (b) are in contrast to the fragmentation patterns observed for the permethylated oligosilanes with a single Fp substituent that one of us has previously published [34]. In such cases considerable Si–Si bond cleavage occurs, including the formation of the disproportionation product $FpSiMe_3$ from $FpSi_2Me_5$. This latter result is an example of the parallel behaviour of $FpSiMe_2SiMe_3$ in both mass spectral fragmentation and solution photochemistry [7a] (eq. 4).

$$[FpSiMe_2SiMe_3]^+ \rightarrow [FpSiMe_3]^+ \tag{4a}$$

$$FpSiMe_2SiMe_3 \xrightarrow{h\nu} FpSiMe_3 \tag{4b}$$

Such parallel behaviour does not occur when two Fp units are bonded to the disilane, *i.e.* $FpSiMe_2SiMe_2Fp$ (*cf.* eq. 3).

Acknowledgements

Support of this research by the National Science Foundation and CONACYT via a USA-Mexico Collaborative Research Award, No. Int-9002051, and establishment of a Minority Research Center of Excellence in Materials Science at the University of Texas at El Paso via Grant RII-88-02973, is acknowledged.

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