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Synthesis and photolysis of the five possible isomeric phenyl-hexamethyltrisilyl-(cyclopentadienyldicarbonyliron) complexes: $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si_3Me_6Ph$ *

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Abstract

Isomeric phenyl-hexamethyltrisilyliron complexes of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si_3Me_6Ph$, $FpSi_3Me_6Ph$ (I–V) have been synthesized, characterized, and photolysed in an inert solvent. Separate photolyses of the linear Fp complexes, *e.g.* $FpSiMe_2SiMe_2SiMe_2Ph$ (III), result in the transient formation of intermediate isomeric 2-substituted trisilyl Fp complexes, $FpSiMe(SiMe_3)(SiMe_2Ph)$ (IV) and $FpSiPh(SiMe_3)_2$ (V) which photodeoligomerize to $FpSiMe_3$ and $FpSiMe_2Ph$ via the intermediacy of Fp disilyl complexes. The product distribution from the photolyses of the Fp complexes is in accord with a mechanism involving equilibrating silyl(silylene) iron complexes. The two branched silyl complexes, $FpSiPh(SiMe_3)_2$ and $FpSiMe(SiMe_3)(SiMe_2Ph)$, isomerize prior to formation of the disilanes whereas the linear trisilanes and disilanes do not interconvert.

1. Introduction

Polysilanes and oligosilanes are useful precursors for photoresists, preceramics and photoconducting materials [1–3]. We have an ongoing interest in transition-metal oligosilanes and polysilanes and recent studies in our own and other laboratories on the photochemistry of oligo- and polysilyl complexes of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$–(Fp) have shown some unique and remarkable transformations (eqns. (1)–(4)) [4–6].

$$\mathrm{FpSiMe_2SiPh_3} \xrightarrow{h\nu} \mathrm{FpSiMe_3} + \mathrm{FpSiMe_2Ph} + \mathrm{FpSiMePh_2} \tag{1}$$

$$\mathrm{FpSiMe_2SiMe_2Fp} \xrightarrow{h\nu} [(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)}]_2 + (\mu\text{-}\mathrm{CO})(\mu\text{-}\mathrm{SiMeSiMe_3}) \xrightarrow{h\nu} [(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)}]_2(\mu\text{-}\mathrm{SiMe_2})_2 \tag{2}$$

$$\mathrm{FpSiMe_2SiMe_2SiMe_3} \xrightarrow{h\nu} \mathrm{FpSiMe(SiMe_3)_2} \xrightarrow{h\nu} \mathrm{FpSiMe_2SiMe_3} \xrightarrow{h\nu} \mathrm{FpSiMe_3} \tag{3}$$

$$\mathrm{FpSiMe_2SiMe_2SiMe_2SiMe_3} \xrightarrow{h\nu} \mathrm{FpSi(SiMe_3)_3} \tag{4}$$

These various reactions proceed via a series of equilibrating silyl(silylene) complexes formed upon α-elimination from a 16 electron transient formed by photoejection of CO from the initial metal complex, *e.g.* $(\eta^5\text{-}C_5H_5)Fe(CO)(=SiR_2)(SiR_3)$. Such intermediates have been observed spectroscopically by Turner *et al.* [7a] and trapped by the Ogino group using a methoxy R group in the initial complexes [7b].

Related 1,3 migrations in silyl(silylene) metal systems have recently been observed by both the Berry and Fink groups [7c,d].

We observed that the related η^5-indenyldicarbonyliron-pentamethyldisilyl and -heptamethyltrisilyl complexes, $(\eta^5\text{-}C_9H_7)Fe(CO)_2$–(IFp), exhibit somewhat differing photochemistry. Photochemical treatment of these complexes in the presence of Ph_3P does not effect an expulsion of the $SiMe_2$ fragment but results in simple phosphine substitution reactions for the disilyl complex, and phosphine substitution coupled with rearrangement for the trisilyl complex (eqns. (5), (6)) [8].

$$\mathrm{IFpSiMe_2SiMe_3} \xrightarrow[\mathrm{PPh_3}]{h\nu} (\eta^5\text{-}\mathrm{C_9H_7})\mathrm{Fe(CO)(PPh_3)SiMe_2SiMe_3} \tag{5}$$

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* Dedicated to Professor Mike Lappert as another outstanding product of Wilson's Grammar School and leader in the arena of group 14 chemistry.

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$$\mathrm{IFpSiMe_2SiMe_2SiMe_3} \xrightarrow[\mathrm{PPh_3}]{h\nu} (\eta^5\text{-}\mathrm{C_9H_7})\mathrm{Fe(CO)(PPh_3)SiMe(SiMe_3)_2} \quad (6)$$

We now report the synthesis, characterization, and photochemistry in inert hydrocarbon solvents, of a series of isomeric trisilyl complexes of the Fp system in which one methyl group has been replaced by a phenyl group, *i.e.* $FpSi_3Me_6Ph$; $FpSiMePhSiMe_2SiMe_3$ (I), $FpSiMe_2SiMePhSiMe_3$ (II), $FpSiMe_2SiMe_2SiMe_2Ph$ (III), $FpSiMe(SiMe_3)(SiMe_2Ph)$ (IV), and $FpSiPh(SiMe_3)_2$ (V).

TABLE 1. Spectroscopic and analytical data for the silanes and complexes [a,b]

$PhMe_2SiSiPhMeSiMe_3$: b.p. 114–116°C/0.10 mmHg	
Anal. Calcd.(Found)	C, 65.82 (65.54); H, 8.52 (8.83)
^1H	0.52 ($SiMe_2$); 0.51 (SiMe); 0.10 ($SiMe_3$); 7.38–7.39, 7.05–7.17 (Ph)
^{13}C	−8.46 (SiMe); −2.59 ($SiMe_2$); −0.96 ($SiMe_3$); 128.0, 128.2, 128.4, 128.8, 134.1, 134.8, 137.1, 139.3 (Ph)
^{29}Si	−15.4 ($SiMe_3$); −18.7 ($SiMe_2$); −46.0 (SiMe)
$ClSiMe_2SiPhMeSiMe_3$: b.p. 105–107°C/0.30 mmHg	
^1H	0.42 ($SiMe_2$); 0.38 (SiMe); 0.16 ($SiMe_3$); 7.13–7.16, 7.41 (Ph)
^{13}C	−1.10 ($SiMe_3$); 3.15 (SiMe); 3.59 ($SiMe_2$); 128.8, 134.1, 134.7, 135.1 (Ph)
^{29}Si	25.4 ($SiMe_2$); −15.5 ($SiMe_3$); −44.6 (SiMe)
$FpSiMePhSiMe_2SiMe_3$ (I)	
Anal. Calcd (found)	C, 53.28 (53.25); H, 6.53 (6.85)
^1H	0.03 ($SiMe_3$), 0.38 ($SiMe_2$), 0.79 (SiMe); 4.08 (C_5H_5); 7.2–7.6 (Ph)
^{13}C	−3.88, −0.97, 3.08 (SiMe); 84.04 (C_5H_5); 129.2, 133.9, 135.3, 147.0 (Ph); 216.0 (CO)
^{29}Si	15.1 (FeSi), −14.8 ($SiMe_3$), −37.6 ($SiMe_2$)
IR: ν(CO)	1997, 1946
Mass (*m/e*, %) [c]	428 (12); 400 (15); 313 (24); 297 (25); 251 (100); 177 (30); 135 (28); 121 (25); 73 (28)
$FpSiMe_2SiMePhSiMe_3$ (II) [d]	
^1H	0.20 ($SiMe_3$); 0.57 (SiMe); 0.70 ($SiMe_2$); 4.00 (C_5H_5); 7.15–7.49 (Ph)
^{13}C	−0.60, 4.86, 6.21 (SiMe); 82.91 (C_5H_5); 128.2, 128.5, 134.6, 140.1 (Ph); 215.9 (CO)
^{29}Si	21.6 (FeSi), −14.5 ($SiMe_3$), −36.9 (SiMePh)
IR: ν(CO)	1997, 1946
Mass (*m/e*, %)	428 (10); 400 (5); 313 (20); 297 (25); 251 (100); 177 (40); 135 (35); 121 (25); 73 (20)
$FpSiMe_2SiMe_2SiMe_2Ph$ (III)	
Anal.Calcd (Found)	C, 53. 28 (53.42); H, 6.53 (6.74)
^1H	0.26 ($SiMe_3$); 0.46 ($SiMe_2$); 0.52 (SiMe); 4.09 (C_5H_5); 7.2–7.5 (Ph)
^{13}C	−3.82, −2.65, 5.11 (SiMe); 83.19 (C_5H_5); 128.60, 128.77, 134.31, 140.42 (Ph); 215.9 (CO)
^{29}Si	21.4 (FeSi), −18.3 ($SiMe_2Ph$), −37.0 ($SiMe_2$)
IR: ν(CO)	1997, 1946
Mass (*m/e*, %)	428 (1); 385 (5); 313 (20); 251 (100); 177 (20); 135 (30); 121 (15); 73 (10)
$FpSiMe(Cl)SiMe_3$	
Anal. Calcd (Found)	C, 40.19 (39.63); H, 5.21 (5.43)
^1H	0.27 ($SiMe_3$), 0.96 (SiMe); 4.18 (C_5H_5)
^{13}C	−1.28 ($SiMe_3$), 9.24 (SiMe); 84.2 (C_5H_5); 213.8, 214.3 (CO)
^{29}Si	80.3 (FeSi), −9.4 ($SiMe_3$)
IR: ν(CO)	2016, 2008, 1969, 1958
$FpSiMe(SiMe_2Ph)SiMe_3$ (IV) [e]	
^1H	0.22, 0.53, 0.58 (Me); 4.09 (C_5H_5); 7.16, 7.51 (Ph)
^{13}C	−3.06, −0.95, 1.08 (Me); 82.7 (C_5H_5); 128.6, 129.4, 134.2, 142.0 (Ph); 215.6 (CO)
^{29}Si	−8.21 ($SiMe_3$), −12.33 (FeSi), −23.27 ($SiMe_2Ph$)
IR: ν(CO)	1997, 1946
Mass (*m/e*, %)	428 (15); 400 (5); 385 (7); 313 (18); 295 (15); 251 (100); 177 (45); 135 (55); 121 (50); 73 (65)
$FpSiPh(SiMe_3)_2$ (V)	
^1H	0.40 ($SiMe_3$); 4.16 (C_5H_5); 7.17, 7.61, 7.77 (Ph)
^{29}Si	−9.5 ($SiMe_3$), −20.0 (FeSi)

[a] NMR spectra were recorded in C_6D_6 and the values are in ppm relative to TMS. [b] IR spectra (cm^{-1}) were recorded in hexane. [c] Mass spectra were recorded on a Hewlett Packard 5890/5971 GC/mass spectrometer. [d] Mixture with slight impurity of complex IV. [e] Mixture with slight impurity of $FpSiMe_3$.

2. Experimental section

All reactions were performed under a nitrogen atmosphere with the use of dry, oxygen free, solvents. Starting silicon materials, Me_2SiCl_2, Me_3SiCl, $Me_3Si\text{-}SiMe_3$, $PhMe_2SiCl$, and $Ph_2MeSiCl$, were purchased from Petrarch Systems Inc. Other starting organosilicon compounds were prepared by the reported procedures; $ClSiMe_2SiMe_3$ [9], $ClSiMe_2SiMe_2Ph$ [10], $ClSiPhMeSiMe_3$ [11], $PhSiMe_2SiMe_2SiMe_2Ph$ [12], $Ph_2SiMeSiMe_2SiMe_3$ [13]; $ClSiMe_2SiMe_2SiMe_2Ph$ was prepared from $PhSiMe_2SiMe_2SiMe_2Ph$ using the $AlCl_3/HCl$ route, as were $ClSiMePhSiMe_2SiMe_3$ and $ClSiMe_2SiPhMeSiMe_3$ (b.p. 105–107°C/0.30 mmHg, 70% yield), two previously unreported compounds which were used directly for transformation to their Fp derivatives; $PhMe_2SiSiPhMeSiMe_3$ was prepared by the reaction between $PhMe_2SiLi$ and $ClSiPhMeSiMe_3$ in 80% yield with full characterization provided in Table 1; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ was purchased from Strem Chemicals, and reagent grade silica gel (grade 950, 60–200 mesh) from MCB Reagents. NMR spectra were recorded on a Bruker NR 200-MHz spectrometer and IR spectra on a Perkin–Elmer 1600 FT IR spectrophotometer. Elemental analyses were performed by Galbraith Laboratories.

Typical experimental procedures are outlined below.

2.1. *Synthesis of $FpSiMePhSiMe_2SiMe_3$*

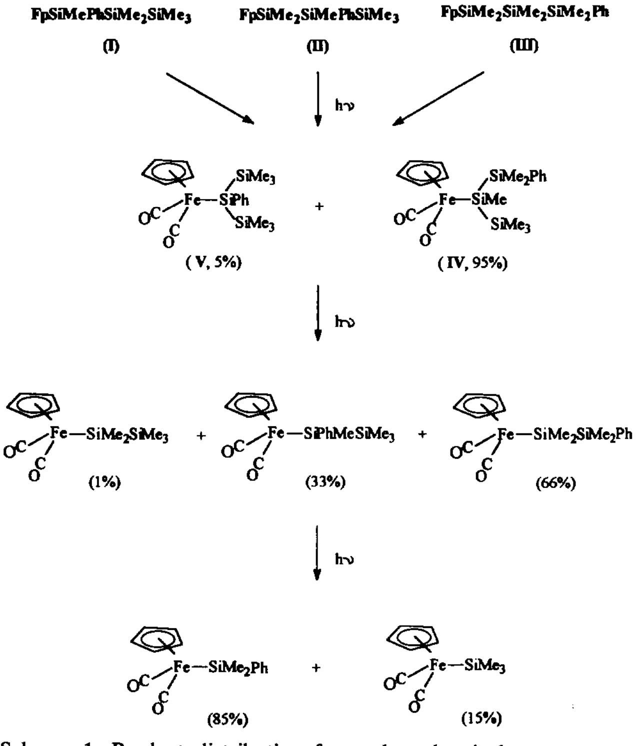
To 75 ml of a THF solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-Na^+$ (prepared from 1.44 g (3.7 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$) was added 2.1 g (7.4 mmol) of $ClMePhSiSiMe_2SiMe_3$ at 0°C. The solution was stirred for 1 h and then permitted to warm to room temperature and further stirred for 4 h. The solvent was then removed *in vacuo* and the residue was extracted with hexane. This solution was concentrated and placed upon a 2.5 cm × 20 cm silica gel column. Elution with the same solvent developed a bright yellow band which was collected to produce 2.6 g (6.1 mmol, 80% yield) of $FpSiMePhSiMe_2SiMe_3$ as an orange oil. Analytical and spectral data are recorded in Table 1.

2.2. *Synthesis of $FpSiMe(Cl)SiMe_3$*

A solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-Na^+$ was prepared from 3.0 g (8.47 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in 75 ml of THF. After the solvent was removed under vacuum for 5 h at 120°C, 100 ml of degassed cyclohexane was added to the solid $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]]^-Na^+$. A solution of 1,1-dichlorotetramethyldisilane (3.16 g, 16.9 mmol) in 60 ml of cyclohexane was added dropwise to the heterogeneous mixture at 0°C. The reaction mixture was vigorously stirred for 3 days at room temperature after which the mixture was filtered through a sintered-glass frit and concentrated under vacuum. The brown residue was purified by molecular distillation with a Kugelrohr (85°C, 0.025 mmHg) to give an orange crystalline compound, yield 3.61 g (65%). (lit. [7b] yield 57%).

2.3. *Synthesis of $FpSiMe(SiPhMe_2)SiMe_3$*

A solution of $PhMe_2SiLi$ (prepared from 0.74 g, 4.33 mmol, of $PhMe_2SiCl$) was added dropwise to 1.4 g (4.26 mmol) of $FpSiMe(Cl)SiMe_3$ in 30 ml of THF at −78°C with vigorous stirring. The reaction mixture was stirred at low temperature for 1 h and then the temperature was allowed to rise to room temperature. The mixture was further stirred for 16 h at room temperature and the volatile materials were removed *in vacuo*. The residue was extracted with 50 ml of hexane and filtered. This procedure separated a considerable amount of $[Fp]_2$ which was not soluble in hexane. The solution was concentrated and placed upon a 2 cm × 25 cm silica gel column and the yellow band formed was eluted with hexane to give 0.2 g of a mixture of $FpSiMe(SiMe_2Ph)SiMe_3$ and $FpSiMe_3$ in the ratio of 80:20. Attempts to purify the desired compound from the mixture were unsuccessful.



Scheme 1. Product distribution from photochemical treatment of complexes I–V.

2.4. Photochemical treatment of the complexes

Photolyses were performed using a 450-W Hanovia 679 Å medium-pressure mercury lamp in two distinct ways. The degassed 10^{-2} M hexane solutions of the complexes, in Pyrex 9820 test tubes, were irradiated and analyses of the products were made using an internal standard method with a Beckman Model 332 HPLC system with UV detector (270 nm). A reverse phase C-18 column, Perkin-Elmer 2580162, was used with a solvent mixture of CH_3CN/H_2O (80:20 v/v). The results of these experiments with product distributions, are recorded in Scheme 1. Separate photolyses were also performed with concentrated solutions of the Fp complexes (0.2 g in 0.5 ml of degassed C_6D_6) and the reactions were followed by ^{29}Si and ^1H NMR spectroscopy. Both methods resulted in equivalent product distributions, which were also verified using GC/mass spectrometry.

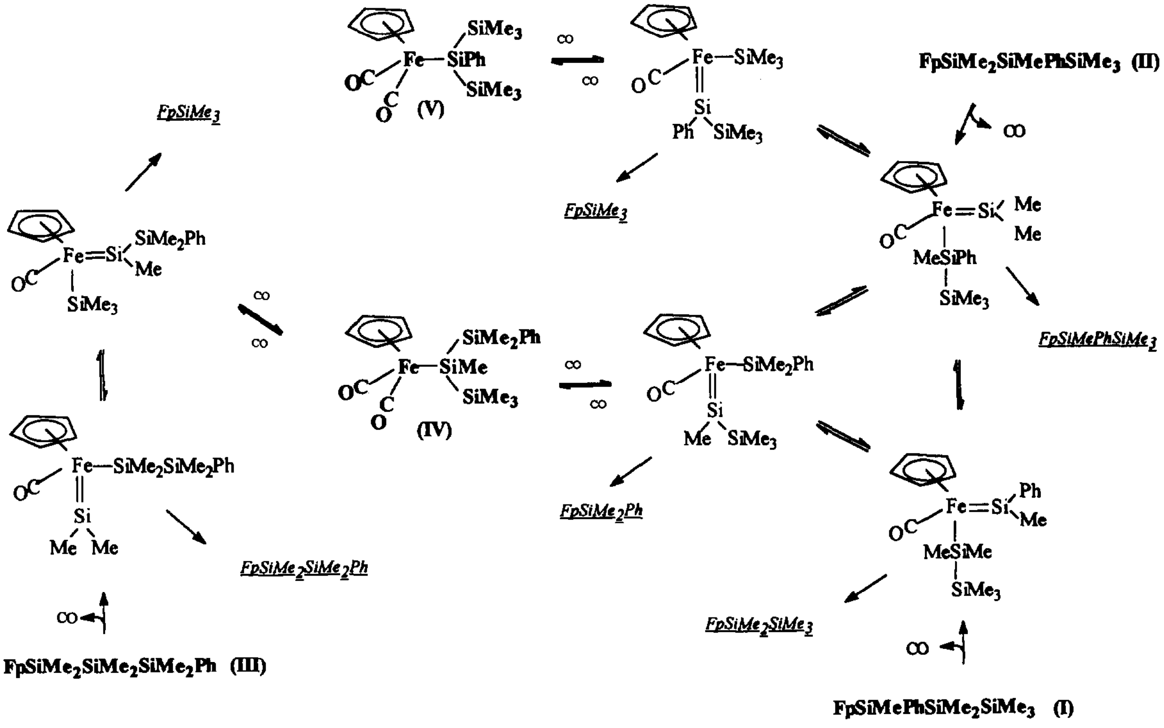
3. Results and discussion

The linear trisilane complexes, $(\eta^5\text{-}C_5H_5)Fe(CO)_2]\text{-}Si_3Me_6Ph$, were prepared in moderate to good yields via the standard salt elimination reaction, an example of which is outlined in eqn. (7) for 3-phenylhexamethyltrisilyl-1-cyclopentadienyldicarbonyliron (III).

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-Na^+ + ClSiMe_2SiMe_2SiMe_2Ph \xrightarrow{THF} [(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2SiMe_2SiMe_2Ph \quad (7)$$

The spectroscopic data of these complexes are recorded in Table 1 and are unexceptional. As usual with transition metal-substituted silanes, ^{29}Si NMR spectroscopy is useful for characterization. The Si atom directly bonded to the iron atom (Si_α) exhibits an approximately 35 ppm downfield chemical shift compared to the methyl analog whereas the corresponding shift for Si_β is 10 ppm, and that for Si_γ 0 ppm [14].

The branched trisilane complex $FpSiPh(SiMe_3)_2$ (V) was readily synthesized by the general route outlined in eqn. (7), and was recently described by West and Pham [15] with the single crystal X-ray structure. However, $FpSiMe(SiMe_2Ph)SiMe_3$ (IV) was only obtained in low yield by the reaction of $PhSiMe_2Li$ with $FpSiMe(Cl)SiMe_3$ along with minor amounts of $FpSiMe_3$, whose mode of formation is unknown, and significant yields of Fp dimer. This result contrasts significantly with other studies in our laboratory [16]



Scheme 2. Mechanism for the photochemical transformations of complexes I–V.

which have shown that when Fp-disilanes with the chloride leaving group on the Si_β atom are allowed to react with group 14 nucleophiles the coupling reaction product is the only product obtained in good yield (eqn. (8)).

$$FpSiMe_2SiMe_2Cl + Ph_3ELi \xrightarrow{THF} FpSiMe_2SiMe_2EPh_3 \quad (8)$$

(E = Si, Ge, Sn)

Complexes **I**–**V** were investigated with respect to their photochemical activity using ^{29}Si NMR, HPLC, and where needed GC/mass spectrometric analysis. Photochemical irradiations of the individual linear trisilane complexes, **I**–**III** (Schemes 1 and 2) were each in accord with the results obtained from related Fp-substituted disilanes and resulted in the ultimate formation of $FpSiMe_3$ and $FpSiMe_2Ph$ in 15% and 85% relative abundances respectively [4c]. However, it was possible to observe the intermediate steps in this deoliogmerization process. For each of **I**, **II**, and **III**, formation of branched trisilane complexes was the initially observed photochemical event. The relative amounts of the two isomers greatly favoured the formation of **IV**, *i.e.* $FpSiMe(SiMe_3)(SiMe_2Ph)$ (95%), *cf.* $FpSiPh(SiMe_3)_2$ (5%). We were unable to observe any evidence, *i.e.* less than 1% abundances by GC/mass spectrometry, for the isomerization of **I**, **II**, or **III**, involving interconversions to each other. Indeed as noted in Scheme 2, such direct interconversion for **III** is not possible without intermediate formation of the branched silane complex **IV**. Continued irradiation led to the intermediacy of the disilyl comlexes $FpSiMe_2SiMe_2Ph$ (66%) and $FpSiMePhSiMe_3$ (33%) with final formation of the Fp-monosilyl complexes. Using GC/mass spectrometry, it was possible to note very low concentrations of $FpSiMe_2SiMe_3$ at less than 2% relative abundances. The deoligomerization of the transient disilanes $FpSiMe_2SiMe_2Ph$ and $FpSiMePhSiMe_3$ are in accord with previously reported data.

Complex **V**, $FpSiPh(SiMe_3)_2$, when photolysed separately led rapidly to the formation of the isomeric complex **IV**, $FpSiMe(SiMe_2Ph)SiMe_3$ prior to continued deoligomerization as noted above. We were unable to observe significant conversion of **IV** to **V** in separate experiments involving photolysis of **IV** as starting material, and only formation of di- and mono-silyl iron complexes was observed. Irradiation of the branched trisilane complexes **IV** and **V** did not result in the formation of the linear trisilanes, *i.e.* the isomerization is a one-way process as may be predicted from thermodynamic considerations.

We have made no attempt to quantitatively assess the relative rates of conversion of the various complexes noted in the photochemical degradation process. However, certain points are very clear from the nature of the observed species, their relative temporal stabilities during photochemistry, and their ability to be observed at all. We assume that the above chemistry occurs *via* mechanisms involving intermediate silyl (silylene) complexes (Scheme 2). The eventual displacement of the silylenes by CO has been complicated by the previous inability to trap such species, the majority of the expelled silicon is transformed to siloxane materials even in the presence of trapping agents. We have recently devised methods to trap some of the silylene as R_2Si and this will be the subject of a manuscript in preparation. With respect to the current study the following conclusions may be presented.

(A) The formation of exactly the same product distribution upon individual irradiation of each of the five complexes **I**–**V** is a verification of the nature of the mechanism involving the rapidly equilibrating silyl(silylene) intermediates via 1,3-migrations from silicon to silicon.

(B) No interconversion of the linear trisilyl complexes **I**, **II**, and **III** was observed, hence re-coordination of CO to the silyl(silylene) complexes of the type $(\eta^5\text{-}C_5H_5)Fe(CO)({=}SiR_2)(SiR_2SiR_3)$, R Me, Ph, does not result in reformation of Si–Si bonds, only elimination of the silylene and formation of Fp-disilanes and/or alkyl/aryl migration to form $(\eta^5\text{-}C_5H_5)Fe(CO)({=}SiRSiR_3)SiR_3$ (Scheme 2).

(C) The rapid and almost exclusive formation of $FpSiMe(SiMe_3)(SiMe_2Ph)$ as the initial photo-product from each of **I**, **II**, and **III** illustrates that the reaction of the silyl(silylene) intermediates of the type $(\eta^5\text{-}C_5H_5)Fe(CO)({=}SiRSiR_3)(SiR_3)$ formed by 1,3-alkyl/aryl migrations from $(\eta^5\text{-}C_5H_5)Fe(CO)({=}SiR_2)(SiR_2SiR_3)$, either immediately isomerize to the branched trisilyl group prior to CO re-coordination, or react with CO to form the trisilyl–Si bonds. The conclusions (B) and (C) require that the iron silylenes with a Si–Si linkage, $Fe{=}SiRSiR_3$, are more resistant to displacement from the metal center than their alkyl- or phenyl-substituted analogs, $Fe{=}SiR_2$. This is also apparent from the isomerizations of longer oligosilyl–Fp complexes described in eqn. (4) where no silylene expulsion occurs.

(D) The participation of the Ph group in the various reactions studied is interesting. The conversion of linear to branched silyl complexes suggests that the relative stabilities of the silyl(silylene) intermediates is enhanced when the aromatic group is further from the Fe atom, *i.e.* in the β position rather than the α position, *i.e.* $Fe{=}SiMeSiMe_3(SiMe_2Ph)$ favoured over $Fe{=}SiPhSiMe_3(SiMe_3)$. For the final elimination of SiR_2 from the disilyl complexes $FpSiMe_2SiMe_2Ph$ and FpSi-

$MePhSiMe_3$, the equilibrium between $Fe{=}SiMe_2(SiMe_2Ph)$ and $Fe{=}SiPhMe(SiMe_3)$ greatly favours the former intermediate, with the Ph group on the silyl, not silylene group. The reasons for these trends are not clear. Simple steric effects could be involved; however, current studies on substituent effects in the series $FpSiMe_2SiMe_2(C_6H_4X)$, $X = CF_3$, NMe_2, Cl, OMe, suggest that more complicated aspects of the chemistry must be considered.

The reasons for the apparent greater stability of metal silylenes that contain a direct Si–Si linkage are unclear. Turner *et al.* have demonstrated that the reaction of the intermediate $(\eta^5\text{-}C_5H_5)Fe(CO)(=SiMe_2)(SiMe_3)$ with CO to eliminate the silylene ligand is a photochemical event. It is possible that the various reactions of iron silylenes with CO leading to formation of Si–Si bonds rather than elimination result from subtle aspects of the optical spectra of the various intermediates changing their photochemical response. It is also possible that the reformation of the silicon–silicon bond in silyl (silylene) intermediates, *e.g.* $(\eta^5\text{-}C_5H_5)Fe(CO)\,(=SiRSiR_3)\,(SiR_3)$, resulting in the formation of $FpSiR(SiR_3)_2$ may not involve the re-coordination of CO prior to, but subsequent to, the Si–Si bond formation and thus relative thermodynamic versus kinetic stability factors are involved. Indeed, given the complexity of such rearrangements as illustrated in eqn. (4), this seems quite possible.

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