in the hydrolysis of cytidine 2′,3′-cyclic monophosphate catalyzed by ribonuclease A.[17] Although the proton inventory method[16] is ambiguous about the precise roles of the protons whose transfers are being detected, one interpretation is that the hydrolysis involves the mechanism of Scheme VIIB in which the last two steps are merged (corresponding to the first two steps of Scheme VIIA), so that two protons are moving.

It should be noted that by this mechanism, and indeed most others, *the enzyme oscillates between two states*. In its resting state His-12 is unprotonated, while His-119 is an imidazolium ion. After the steps of Scheme VIIA, which produce the cyclic phosphate product, the enzyme protonation states are reversed. The new base/acid pair is now ideally set up to perform the steps of Scheme VIIB, hydrolysis of the cyclic phosphate, that will return the enzyme to its original state. This may explain why the resting enzyme is not[18] an outstanding catalyst for the hydrolysis of added cyclic phosphate substrates: it has not been put into the correct state of protonation by the reactions of Scheme VIIA. Such oscillation in catalyst structure accompanying multistep reactions can be invoked for many other enzymes as well.

The mechanism of Scheme VII, possibly with steps 1 and 2 merged, is consistent with everything known about the enzyme so far. It also takes advantage of the catalytic effects we have seen in our model studies. Thus, at this time we consider Scheme VII to be the most likely enzyme mechanism; it directly parallels Scheme V for the model system. As with carboxypeptidase A,[19] a model system has given us additional insight into the probable details of the enzymatic process.

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Registry No. (3′,5′)-UpU, 2415-43-2; (2′,5′)-UpU, 13493-13-5; uridine, 58-96-8; 2′,3′-cyclic uridine monophosphate, 606-02-0; imidazole, 288-32-4; imidazole HCl, 1467-16-9; ribonuclease, 9001-99-4.

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Synthesis and Photochemical Deoligomerizations of a Series of Isomeric Disilyliron Complexes: $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si_2Ph_{3-n}Me_{2+n}$[1]

Keith H. Pannell,* James M. Rozell, Jr., and Carlos Hernandez

Contribution from the Department of Chemistry, University of Texas at El Paso,
El Paso, Texas 79968. *Received August 22, 1988*

Abstract: A series of six disilyl complexes of the general type $(\eta^5\text{-}C_5H_5)Fe(CO)_2Si_2Ph_{3-n}Me_{2+n}$, representing three isomeric pairs, have been synthesized and characterized. Photolysis of each complex leads to the formation of a series of monosilyl complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiPh_{3-n}Me_n$ via a silylene expulsion process. The product distribution from photolysis of the isomeric pairs validates a mechanism involving intermediacy of dynamically equilibrating silyl(silylene) complexes.

The interactions of transition-metal complexes with silanes has long been an area of interest involving both stoichiometric and catalytic transformations of the silicon compounds. Many silyl transition-metal complexes are known including σ- and π-bonded organosilyl and silyl groups.[2-4] The particular interaction of oligosilanes with metal complexes has been longstanding,[5-10] with a particular recent resurgence of interest due to the potential of polysilanes as preceramic, photoresist, and photoconducting materials.[11-13]

Previous studies in our laboratories showed that oligosilane derivatives of the transition metals are readily synthesized from the transition-metal systems $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ (Fp),[5,8,14] $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]^-$ (Rp), and $[Re(CO)_5]^-$.[10] Malisch et al. have reported the related $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ systems,[6] and Nicholson et al. have reported $[Mn(CO)_5]^-$ complexes.[7] The results of these studies indicate that the oligosilane complexes may be thermally and oxidatively stable (Fe, Ru, Re) or unstable (Mo).

Of particular interest are the results of photochemical treatment of the Fp complexes where facile deoligomerizations yield, inter alia, monosilyl complexes (eq 1, 2).[8]

$$\mathrm{FpSiMe_2SiMe_3} \xrightarrow{h\nu} \mathrm{FpSiMe_3} + \text{polymer} \qquad (1)$$

$$\mathrm{FpSiMe_2SiPh_3} \xrightarrow{h\nu} \underset{85\%}{\mathrm{FpSiPh_2Me}} + \underset{8\%}{\mathrm{FpSiMe_2Ph}} + \underset{7\%}{\mathrm{FpSiPh_3}} + \text{polymer} \qquad (2)$$

These studies suggested a mechanism involving initial photochemical expulsion of CO to produce a 16e iron complex followed

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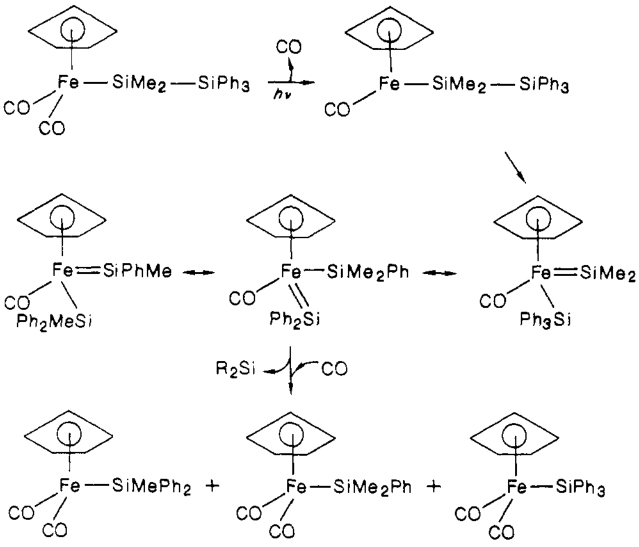
Table I. Yields and Analytical Data for New Compounds

complex	yield, %	anal. found (calcd) C	anal. found (calcd) H	mp [bp][a]
$FpSiMe_2SiPh_3$	70	65.4 (65.6)	5.39 (5.30)	155
$FpSiMePhSiMePh_2$	20[b]	65.8 (65.6)	5.40 (5.30)	oil
$FpSiMe_2SiMePh_2$	65	61.5 (61.1)	5.56 (5.59)	77–80
$FpSiMePhSiMe_2Ph$	51	61.3 (61.1)	5.95 (5.59)	oil
$FpSiMe_2SiMe_2Ph$	62	55.7 (55.1)	5.98 (5.99)	36–8
$FpSiMePhSiMe_3$	75	55.6 (55.1)	6.18 (5.99)	oil
$Ph_2MeSiSiMe_2Cl$	71	62.0 (61.9)	6.62 (6.58)	[106–8 (0.2 mmHg)]
$Ph_2MeSiSiMe_2H$	74	69.9 (70.2)	7.87 (7.86)	[90–2 (0.1 mm)]
$Ph_2MeSiSiMePhH$	45	75.3 (75.4)	7.13 (6.96)	[156–8 (0.2 mm)]
$PhMe_2SiSiMePhH$	49			[104–5 (0.2 mm)]
$PhMe_2SiSiMePhCl$	57	61.7 (62.0)	6.76 (6.62)	[102–4 (0.1 mm)]

[a] Mp in °C; [bp] in °C (mmHg). [b] Yield based upon $Ph_2MeSiSiPhMeH$, which was transformed to the corresponding iodide via direct iodination in CCl_4 and used directly without purification.

Scheme I



by silyl group migration to form a transient silyl(silylene)metal complex intermediate (Scheme I).[8] Following a series of 1,3-alkyl(aryl) migrations, an equilibrium mixture of isomeric 18e intermediates is formed. Finally recoordination of CO yields the appropriate mixture of monosilyl complexes.

If this mechanism is correct, entry into the dynamic equilibrium mixture from any starting complex should produce the same product distribution of monosilyliron complexes. It is the object of this article to report the synthesis of a series of isomeric pairs of $FpSi_2$ complexes ($FpSiMe_2SiPh_3$ (I) and $FpSiMePhSiMePh_2$ (II), $FpSiMe_2SiMePh_2$ (III) and $FpSiMePhSiMe_2Ph$ (IV), and $FpSiMe_2SiMe_2Ph$ (V) and $FpSiMePhSiMe_3$ (VI)), coupled with the results of their photochemical transformation into a series of monosilyl complexes, $FpSiMe_3$, $FpSiMe_2Ph$, $FpSiMePh_2$, and $FpSiPh_3$.

Experimental Section

All reactions were performed in a dry N_2 atmosphere with dry, oxygen-free solvents. Starting silicon compounds, Me_2SiHCl, $PhMeHSiCl$, $Me_2PhSiCl$, $MePh_2SiCl$, and Ph_3SiCl, were purchased from Petrarch Systems. The disilanes $PhMe_2SiSiMe_2Cl$ and $Me_3SiSiPhMeCl$ were prepared by published procedures:[15,16] $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ was purchased from Strem Chemicals.

NMR spectra were recorded on a Bruker NR 200-MHz spectrometer and IR spectra on a Perkin-Elmer 580B spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Synthesis of Disilylhydrides, $Ph_{3-n}Me_{2+n}Si_2H$. The general synthetic procedure involving treatment of $Ph_nMe_{3-n}SiLi$ with the appropriate $Ph_nMe_{2-n}SiHCl$ was used for the synthesis of the disilanes. The specific synthesis of $MePh_2SiSiMePhH$ is described below as typical of all syntheses.

A Schlenk flask was charged with 9.8 g (42 mmol) of $MePh_2SiCl$, 80 mL of THF, and 0.8 g (115 mmol) of Li. The mixture was magnetically stirred for 24 h after which time the color had changed to the characteristic greenish black of $MePh_2SiLi$.

A separate flask equipped with a magnetic stirring bar and addition funnel was charged with 6.6 g (42 mmol) of $MePhSiHCl$ and 20 mL of THF. This solution was cooled to 0 °C and the $MePh_2SiLi$ solution from above was added dropwise via the addition funnel. Upon complete addition the solution was permitted to warm to room temperature and stirred for an additional 4 h. The solvent was removed under reduced pressure and hexane added to dissolve the products. The hexane solution was filtered and the filtered material washed with an extra 50 mL of hexane. The hexane fractions were concentrated under reduced pressure, and final distillation produced 6.1 g (45%) of the product, bp 156–158 °C (0.2 mmHg). Analytical and spectral data for the compound are recorded in Tables I and II.

Halogenation of Disilylhydrides. Direct halogenation was employed for all the silanes used in this study. A synthetic example is described below involving a typical chlorination.

Synthesis of $Ph_2MeSiSiMe_2Cl$. Under a nitrogen atmosphere, Cl_2, used directly from a lecture cylinder, was bubbled into a cooled (0 °C) solution of $Ph_2MeSiSiMe_2H$, 9.3 g (36.3 mmol) in 50 mL of $CHCl_3$. The reaction was monitored by infrared spectroscopy, specifically observing the Si-H frequency at 2102 cm^{-1}. When this band had disappeared, approximately 25 min, the solvent was removed under reduced pressure and the resulting liquid fractionally distilled to give $Ph_2MeSiSiMe_2Cl$, 7.5 g (25.8 mmol, 71%), bp 106–108 °C (0.2 mmHg). Spectral and analytical properties are recorded in Tables I and II.

Synthesis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2Ph_{3-n}Me_{n+2}Si_2$. As a typical example of the general procedure, the synthesis of $FpSiMePhSiMe_2Ph$ is described.

To 50 mL of a cooled (0 °C) solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-Na^+$ prepared by literature procedure[17,18] from 1.24 g (3.5 mmol) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ was added 2.0 g (6.9 mmol) of $Me_2PhSiSiMePhCl$. The solution was stirred for 90 min and permitted to warm to room temperature. The solvent was removed under vacuum and the residue extracted in an 85:15 hexane/methylene chloride solvent mixture. This solution was concentrated and then placed upon a 2.5 × 20 cm silica gel column. Elution with the same solvent mixture developed a bright yellow band, which was collected to produce 1.5 g (17.9 mmol, 51% based upon $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$) of $FpSiMePhSiMe_2Ph$ as an orange oil. Analytical and spectral properties are recorded in Tables I and II.

Photochemical Treatment of $FpSi_2Ph_{3-n}Me_{n+2}$ Complexes. Photolyses were performed using a 450-W Hanovia 679A medium-pressure mercury lamp on degassed 10^{-2} M cyclohexane solutions of the complexes in Pyrex 9820 test tubes for 1 h. Analyses of product yields and distributions 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 258 0162, was used with a solvent mixture of 65:35 (v/v) CH_3CN/H_2O. The results of such experiments with percent transformation of the starting Fp complex, and the product distributions, are recorded in Table III. The various FpSi complexes were synthesized by published procedures to authenticate the complexes.

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Table II. Spectral Data of the FpSi$_2$Me$_{n+2}$Ph$_{3-n}$[a]

	FpSiMe$_2$SiPh$_3$ (I)
^{13}C	6.18 (SiMe$_2$), 83.6 (C$_5$H$_5$), 128.6, 129.4, 137.0, 137.7 (Ph), 216.2 (CO)
^{1}H	0.56 (SiMe$_2$), 4.47 (C$_5$H$_5$), 7.2–7.7 (Ph)
^{29}Si	−15.4 (SiPh$_3$), 16.8 (FeSiMe$_2$)
ν(CO)	2000, 1948
	FpSiMePhSiMePh$_2$ (II)
^{13}C	−2.67, 2.40 (SiMe), 83.6 (C$_5$H$_5$), 127.4, 127.7, 128.6, 134.1, 135.1, 135.2, 138.3, 138.7, 145.0 (Ph), 214.9, 215.2 (CO)
^{1}H	0.72, 0.77 (SiMe), 4.46 (C$_5$H$_5$), 7.2–7.7 (Ph)
^{29}Si	−16.0 (SiMePh$_2$), 12.2 (FeSiMePh)
ν(CO)	2003, 1950
	FpSiMe$_2$SiMePh$_2$ (III)
^{13}C	−3.82, 4.19 (SiMe), 83.0 (C$_5$H$_5$), 127.9, 128.6, 134.7, 138.7 (Ph), 215.3 (CO)
^{1}H	0.50 (SiMe$_2$), 0.76 (SiMe), 4.46 (C$_5$H$_5$), 7.2–7.7 (Ph)
^{29}Si	−18.2 (SiMePh$_2$), 17.0 (FeSiMePh)
ν(CO)	1999, 1946
	FpSiMePhSiMe$_2$Ph (IV)
^{13}C	−2.33, −2.11, 1.51 (SiMe), 83.7 (C$_5$H$_5$), 127.4, 127.5, 127.6, 128.3, 133.8, 133.9 (Ph), 215.1, 215.2 (CO)
^{1}H	0.45, 0.52, 0.67 (SiMe), 4.51 (C$_5$H$_5$), 7.2–7.7 (Ph)
^{29}Si	−15.4 (SiMe$_2$Ph), 12.3 (FeSiMePh)
ν(CO)	2003 (sh), 1998, 1947
	FpSiMe$_2$SiMe$_2$Ph (V)
^{13}C	−2.8, 3.3 (SiMe), 83.0 (C$_5$H$_5$), 127.8, 128.3, 133.7, 141.3 (Ph), 215.2 (CO)
^{1}H	0.43, 0.45 (SiMe), 4.52 (C$_5$H$_5$), 7.2–7.7 (Ph)
^{29}Si	−15.0 (SiMe$_2$Ph), 16.9 (FeSiMe$_2$)
ν(CO)	1998, 1945
	FpSiMePhSiMe$_3$ (VI)
^{13}C	−0.3, 1.2 (SiMe), 83.9 (C$_5$H$_5$), 127.4, 133.6, 145.8, (Ph), 215.4 (CO)
^{1}H	0.15 (SiMe$_3$), 0.65 (SiMe), 4.60 (C$_5$H$_5$), 7.2–7.7 (Ph)
^{29}Si	−11.6 (SiMe$_3$), 12.7 (FeSiMePh)
ν(CO)	2003 (sh), 1998, 1946
	MePh$_2$SiSiMe$_2$Cl
^{13}C	−5.3, 2.7 (SiMe), 128.1, 129.4, 134.9 (Ph)
^{1}H	0.61 (SiMe$_2$), 0.81 (SiMe), 7.45, 7.64 (Ph)
^{29}Si	−23.4 (SiMe$_2$Ph), 21.7 (SiCl)
	MePh$_2$SiSiMe$_2$H
^{13}C	−6.3, −4.6 (SiMe), 128.0, 128.7, 134.8, 136.9 (Ph)
^{1}H	0.3 (d, J = 4.5 Hz, SiMe$_2$H), 0.75 (SiMe), 4.11 (sept, J = 4.5 Hz, SiH), 7.44, 7.61 (Ph)
^{29}Si	−39.7 (SiMe$_2$H), −21.2 (SiMePh$_2$)
ν(SiH)	2102
	MePh$_2$SiSiMePhH
^{13}C	−7.55, −4.43 (SiMe), 127.8, 127.9, 128.9, 129.0, 134.9, 136.3 (Ph)
^{1}H	0.58 (d, J = 4.6 Hz, SiMeH), 0.76 (SiMe), 4.68 (q, J = 4.6 Hz, SiH), 7.44, 7.59 (Ph)
^{29}Si	−36.9 (SiMeH), −21.8 (SiMePh$_2$)
ν(SiH)	2105
	Me$_2$PhSiSiMePhH
^{13}C	−7.97, −3.57, −3.35 (SiMe), 127.8, 128.7, 133.9, 134.7, 135.2, 138.4 (Ph)
^{1}H	0.336 (SiMe$_2$), 0.339 (d, J = 4.6 Hz, SiMeH), 4.57 (q, J = 4.6 Hz, SiH), 7.16, 7.44 (Ph)
^{29}Si	−35.6 (SiMePhH), −20.8 (SiMe$_2$Ph)
ν(SiH)	2101
	Me$_2$PhSiSiMePhCl
^{13}C	−4.4 (SiMe$_2$), 0.7 (SiMeCl), 128.0, 129.1, 129.7, 133.5, 134.0, 135.9, 136.3 (Ph)
^{1}H	0.54, 0.59, 0.79 (SiMe), 7.45, 7.56 (Ph)
^{29}Si	−21.1 (SiMe$_2$Ph), 12.4 (SiCl)

[a] NMR spectra recorded in CDCl$_3$ with the exception of the Fp complexes whose ^{29}Si NMR were recorded in C$_6$D$_6$. The ^{13}C spectrum of complex I and ^{1}H spectrum of Me$_2$PhSiSiMePhH were also recorded in C$_6$D$_6$. [b] IR spectra recorded in hexane.

Table III. Product Distribution from Photolysis of Complexes FpSi$_2$Me$_{n+2}$Ph$_{3-n}$

	product distribution			
complex	FpSiMe$_3$	FpSiMe$_2$Ph	FpSiMePh$_2$	FpSiPh$_3$
FpSiMe$_2$SiPh$_3$		7	86	7
FpSiMePhSiMePh$_2$		5	89	6
FpSiMe$_2$SiMePh$_2$	1	51	47	
FpSiMePhSiMe$_2$Ph	2	46	53	
FpSiMe$_2$SiMe$_2$Ph	7	93		
FpSiMePhSiMe$_3$	8	92		

[a] These studies are the result of reactions that were 51–60% completed, with overall yields between 50 and 80%.

Separate photolyses were also performed with concentrated solutions of the Fp complexes, 0.1 g in 0.4 of C$_6$D$_6$, and the reactions were followed by ^{29}Si and ^{13}C NMR for further proof of the formation of the various monosilyl complexes.

Results and Discussion

The various complexes (η^5-C$_5$H$_5$)Fe(CO)$_2$Si$_2$Ph$_{3-n}$Me$_{2+n}$ were synthesized by the general reaction described in eq 3.

$$[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]^-\text{Na}^+ + \text{Ph}_{3-n}\text{Me}_{2+n}\text{Si}_2\text{Cl} \xrightarrow{\text{THF}} (\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\text{Si}_2\text{Ph}_{3-n}\text{Me}_{2+n} \quad (3)$$

The corresponding methylphenylchlorodisilanes were either synthesized by published procedures[15,16] or via the general route described in eq 4 for Ph$_2$SiMeSiMe$_2$Cl.

$$\text{Ph}_2\text{MeSi}^-\text{Li}^+ + \text{Me}_2\text{SiHCl} \rightarrow \text{Ph}_2\text{MeSiSiMe}_2\text{H} \xrightarrow{\text{Cl}_2} \text{Ph}_2\text{MeSiSiMe}_2\text{Cl} \quad (4)$$

Full spectral and analytical data for all silanes and iron silyl complexes are recorded in Tables I and II. All data are consistent with the various formulations.

The ^{29}Si NMR data on the complexes is particularly useful and diagnostic with respect to structural assignments. Each of the disilyl complexes exhibit two resonances, one between 17 and 12 ppm and another between −11 and −19 ppm. The former is due to the silicon atom directly bonded to the Fe atom and is shifted approximately 30 ppm to lower field when compared to the parent methylated disilane, i.e. FpSi$_2$Ph$_{3-n}$Me$_{2+n}$ versus MeSi$_2$Ph$_{3-n}$Me$_{2+n}$, and the latter is due to the second silyl group, which represents a shift to lower field of approximately 7 ppm compared to the methylated disilane. Such shifts are typical of the ^{29}Si chemical shifts of oligosilane derivatives of the Fp system.[19]

The underlying principle in this study is that entry into the mixture of dynamically equilibrating 18e silyl(silylene)iron complexes at any position will generate the same product distribution of monosilyliron complexes upon the displacement of the SiR$_2$ species by CO according to the mechanism in Scheme I. Thus, photolysis of FpSiMe$_2$SiMePh$_2$ will initially lead to the formation of (η^5-C$_5$H$_5$)Fe(CO)(=SiMe$_2$)SiMePh$_2$, while photolysis of FpSiMePhSiMe$_2$Ph will initially produce (η^5-C$_5$H$_5$)Fe(CO)(=SiMePh)SiMe$_2$Ph. Subsequent to formation of these intermediates, the series of 1,3 alkyl/aryl shifts produce the equilibrium mixture of both of these complexes plus (η^5-C$_5$H$_5$)Fe(CO)(=SiPh$_2$)SiMe$_3$. Reaction of these three intermediates with CO will produce the appropriate amounts of FpSiMe$_3$, FpSiMe$_2$Ph, and FpSiMePh$_2$. If the mechanism is correct, the relative amounts of the three monosilyl complexes will be the same regardless of which isomer was photolyzed, e.g. Scheme II.

Photolysis of the various complexes was performed in cyclohexane, and the reaction monitored by ^{1}H and ^{29}Si NMR and

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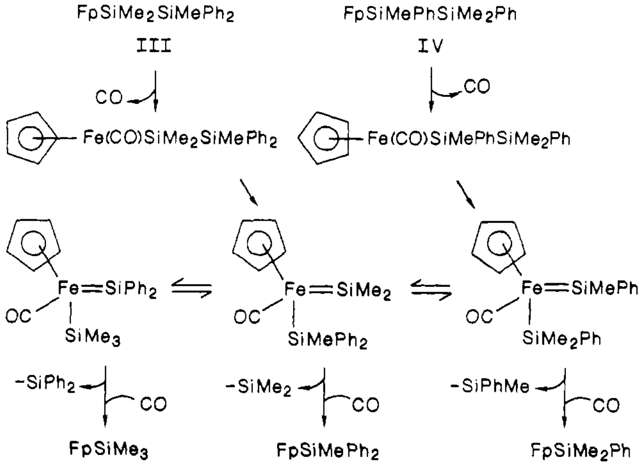
(19) Pannell, K. H.; Bassindale, A. R. *J. Organomet. Chem.* **1982**, *229*, 1

Scheme II



reverse-phase HPLC using a C_{18} column eluting with a 65:35 CH_3CN/H_2O solvent mixture. Photolysis of complex III produced the following relative yields (±3%): $FpSiMe_3$ (1%), $FpSiMe_2Ph$ (46%), and $FpSiMePh_2$ (53%). Photolysis of complex IV yields the same complexes in 2, 51, and 47%, respectively. Photolysis of the other pairs of $FpSi_2$ isomers, I, II and V, VI, results in similarly equivalent product distributions as presented in Table III. The nonstatistical distribution of FpSi complexes suggests either a thermodynamic or kinetic stability difference between the equilibrating 18e silyl(silylene) complexes. The data recorded in Table III do not provide a clear insight to the controlling factors.

The results presented above are consistent with our proposed equilibrating silyl(silylene) intermediates. The isolation and X-ray structural characterization of such a complex has recently been accomplished, lending further credence to such intermediates.[20]

Photochemical irradiation of the $FpSi_2$ complexes in the presence of CO led to lower conversions (5–10% lower) of the disilyl complexes and enhanced yields (5% increase) of the monosilyl complexes after 1-h irradiation. This is consistent with the initial photochemical expulsion of CO from the disilyl complexes since excess CO will promote the reverse reaction. Increased overall yields suggest that potential decomposition of the monosilyl complexes proceeding via CO elimination are retarded. A control reaction, which involved irradiation under identical conditions, of the FpSi complexes, $FpSiMe_3$, $FpSiMe_2Ph$, $FpSiMePh_2$, and $FpSiPh_3$, showed that there is no *preferential* decomposition of these complexes. Prolonged irradiation, in excess of 24 h, of the FpSi complexes yielded $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ as the only iron-containing complex; however, irradiations for 1 h, the identical conditions to those employed in the photolysis of the disilyl complexes, only yielded small amounts of this complex as determined by infrared spectroscopy. The observed relative yields of the monosilyl complexes are a true representation of the direct product yields.

Using both HPLC and NMR techniques, we studied the various reaction products of the photolyses of the $FpSi_2$ complexes to establish the presence or absence of any isomerization of the complexes. We found no evidence for such isomerizations; e.g., photochemical treatment of $FpSiMe_2SiPh_3$ did not provide evidence for the formation of $FpSiMePhSiMe_2Ph$. In terms of the proposed mechanism this finding suggests that subsequent to the initial cleavage of the Si–Si bond and silyl migration to form the silyl(silylene) intermediates recoordination of CO cannot drive the reactions backwards; only release of SiR_2 fragments occurs. This finding is in opposition to results obtained in our laboratory from the photolysis of Fp permethylated oligosilanes containing three or more silicon atoms. For example, photolysis of $Fp(SiMe_2)_3SiMe_3$ resulted in the formation of $FpSi(SiMe_3)_3$ signifying that re-formation of the silicon–silicon bond occurs upon recoordination of CO with no loss of SiR_2 fragments.[21]

The modification of the chemistry of oligosilanes by transition-metal substituents clearly depends upon both the specific metal complex and the various substituents on silicon.

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Registry No. $FpSiMe_2SiPh_3$, 87882-62-0; $FpSiMePhSiMePh_2$, 120547-07-1; $FpSiMe_2SiMePh_2$, 120547-08-2; $FpSiMePhSiMe_2Ph$, 120547-09-3; $FpSiMe_2SiMe_2Ph$, 120547-10-6; $FpSiMePhSiMe_3$, 120547-11-7; $FpSiMe_3$, 31811-63-9; $FpSiMe_2Ph$, 41680-29-9; $FpSiMePh_2$, 41619-97-0; $FpSiPh_3$, 36835-55-9; Fp^-Na^+, 12152-20-4; $Ph_2MeSiSiMe_2Cl$, 118851-97-1; $Ph_2MeSiSiMe_2H$, 120547-04-8; $Ph_2MeSiSiMePhH$, 120547-05-9; $PhMe_2SiSiMePhH$, 120547-06-0; $PhMe_2SiSiMePhCl$, 118851-96-0; $MePh_2SiLi$, 3839-30-3; $MePhSiHCl$, 1631-82-9; $PhMe_2SiLi$, 3839-31-4; $Ph_3SiSiMe_2Cl$, 69397-62-2; Me_2SiHCl, 1066-35-9; $PhMe_2SiSiMe_2Cl$, 941-15-1; $Me_3SiSiPhMeCl$, 33559-14-7.

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