Polysilane–Metal Interactions. Photochemical Deoligomerizations and Base Treatment Migrations from Iron to Cyclopentadienyl Ligands[1]

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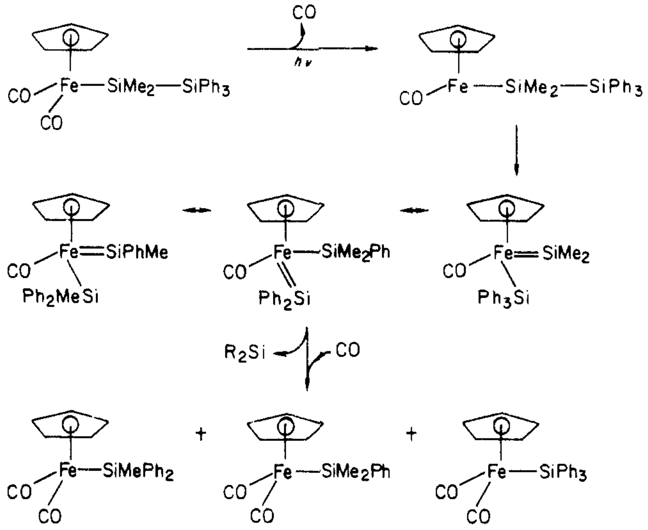
Summary: Iron (Fp) derivatives of polysilanes have been shown to deoligomerize photochemically to yield monosilyl iron complexes and to migrate from iron to the cyclopentadienyl ligand upon treatment with *n*-butyllithium. The migratory aptitude of various polysilanes has been determined. Photochemical treatment of the migrated products does not lead to deoligomerization. Infrared and ^{29}Si NMR data are reported.

There is considerable current interest in the chemical and physical properties of polysilanes by virtue of their potential and actual use as photoresist materials.[2-4] We are currently studying various metal-substituted derivatives of such compounds in an attempt to modify these properties.

One particular system that we have studied is (η^5-C_5H_5)Fe(CO)$_2$–(SiR$_2$)$_n$–SiR$_3$ (Fp–(Si)$_n$), which we have shown to be thermally stable but extremely labile photochemically with respect to depolymerization. For example, irradiation of a hexane solution of Fp–SiMe$_2$SiMe$_2$SiMe$_3$ with a 500-W Hanovia high-pressure lamp leads smoothly to the isolation of Fp–SiMe$_3$ (80%) and an unidentified polymeric material containing SiOSi and SiOC linkages as determined by infrared and ^{29}Si NMR spectroscopy. The mechanism of this process is not clear. When the substituted disilyl iron complex Fp–SiMe$_2$SiPh$_3$[5] is subjected to the same irradiation, a mixture of the three monosilyl complexes, Fp–SiPh$_2$Me (85%), Fp–SiPhMe$_2$ (7%), and Fp–SiPh$_3$ (8%), is obtained. The relative amounts were determined by HPLC using an alumina column and a chloroform/hexane (4:96) eluent, by comparison with authentic samples.[6] From such a result it is clear that the mechanism is complex, possibly involving silene metal intermediates. A possible mechanism is outlined in Scheme I in which a thermodynamic equilibrium is established of (silylsilene)metal complexes from which expulsion of the R$_2$Si species occurs to yield the observed Fp–SiR$_3$ complexes. The 1,3 migration of groups is reminiscent of related migrations reported for silaolefin isomerizations, e.g., (R$_3$Si)$_2$C=SiRR′ $\rightleftharpoons$ (R$_3$Si)(R$_2$R′Si)-C=SiR$_2$.[7]

Scheme I



Attempts to trap potential SiR$_2$ species have not, to date, been successful, in part due to the ever presence of free CO in the photochemical procedure, which apparently traps whatever transients are generated.

As part of our investigation into the chemical properties of these complexes we have examined their reactivity toward various bases such as *n*-butyllithium. This stems from a report by Berryhill and co-workers that treatment of monosilyl complexes of the Fp system with this reagent results in the deprotonation of the cyclopentadienyl ring, followed by silyl group migration leading to the formation of (η^5-SiC$_5$H$_4$)Fe(CO)$_2^-$ (SiFp$^-$). The latter may be trapped by addition of alkyl halides to generate the corresponding SiFp–alkyl complexes.[8] Treatment of various Fp–polysilyl complexes with *n*-butyllithium in THF results in similar migrations with no evidence for any products resulting from the cleavage of the polysilane backbone. This ability to migrate whole polysilyl groups from metal centers to other ligands offers the potential for simple one-step transformations of polysilanes in such interesting new environments.

In a typical reaction, 1.5 g (4.0 mmol) of Fp–Si$_2$Me$_5$ in THF was treated with a 2-fold excess on *n*-butyllithium at −78 °C. The mixture was stirred for at least 2 h during which time the color changed from yellow to orange. At this time an excess of methyl iodide was added and the mixture allowed to warm to room temperature. The solvent was removed under reduced pressure and the product was extracted with hexane and purified by column chromatography (alumina). The yellow band was eluted with hexane to yield (η^5-Me$_5$Si$_2$C$_5$H$_4$)Fe(CO)$_2$–Me (70%). Anal. Calcd: C, 48.4; H, 6.83. Found: C, 48.5; H, 6.97. Spectral data are recorded in Table I along with those data for representative complexes synthesized by this general route.

If the polysilyl group is separated from the iron atom by a methylene group, i.e., Fp–CH$_2$SiMe$_2$SiMe$_3$,[9] no migration of the silylmethyl group occurs, and quenching of the anion generated by the base treatment with methyl iodide yields the methylcyclopentadienyl iron complex (η^5-MeC$_5$H$_4$)Fe(CO)$_2$–CH$_2$SiMe$_2$SiMe$_3$.

Preliminary competition experiments have been performed to evaluate the relative migratory aptitudes of the polysilyl groups, using a mixture of two complexes with a deficiency of *n*-butyllithium. The reaction mixture was

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[1] Part 12 of "Organometalloidal Derivatives of The Transition Metals". For part 11 see ref 5.

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Table I. Spectral Properties of the Complexes $(RC_5H_4)Fe(CO)_2CH_3$[a]

R	^{29}Si (δ) α	β	γ	^{13}C (δ) SiCH_3 α	β	γ	Fe+CH_3
Me_3Si	−4.1			−0.56			−23.3
Me_3SiMe_2Si	−22.6	−19.0		−3.5	−2.4		−23.1
$Me_3SiMe_2SiMe_2Si$	−19.5	−48.1	−15.1	−2.6	−8.04	−6.7	−22.5
$(Me_3Si)_2MeSi$	−48.2	−15.7		−0.9	−1.37		−22.4
Ph_3SiMe_2Si	−21.5	−22.5		−1.88			−22.5
Ph_3GeMe_2Si	−15.7			−1.52			−22.4
$(CH_3C_5H_4)Fe(CO)_2CH_2Si_2Me_5$	−6.3	−19.9		−1.70	−0.46		−24.0

[a] All the complexes exhibited two CO stretching frequencies at 2010 and 1955 (±1.0) cm^{-1}, and the expected set of ^{13}C resonances for the substituted cyclopentadienyl ring in the range 85–92 ppm. Solvents used were C_6D_6 (NMR) and hexane (infrared).

Table II

	δ($FpSi_n$) − δ($MeSi_n$) α	β	γ	δ(Si_nFpMe) − δ(Si_nMe) α	β	γ
Me_3Si	41.3			−4.1		
Me_5Si_2	36.5	8.3		−3.2	0.4	
Me_7Si_3	37.2	12.0	0.8	−3.8	0.6	0.0

analyzed by using ^{13}C NMR in both the cyclopentadienyl and methyl carbon regions of the spectra. From such results the following two independent sets of order are obtained: $Fp–SiMe_3 < Fp–Si_2Me_5 \leq Fp–Si_3Me_7 < Fp–SiMe(SiMe_3)_2$, and $Fp–SiMe_2GePh_3 < Fp–SiMe_2SiPh_3$. These aptitudes suggest that both the release of steric contraints at the metal center upon migration, $FpSi_1 < FpSi_3 < FpSi(Si)_2$, and electronic factors, $Fp–SiMe_2GePh_3 < Fp–SiMe_2SiPh_3$, are involved. In the case of the latter two complexes the Si–Fe bond is significantly longer in the disilyl complex than in the silylgermyl complex, 2.346 vs. 2.328 Å, presumably due to the greater electron-donating capacity of the silylgermyl complex.[5,10] This suggests that the stronger Si–Fe bond in the silylgermyl complex results in the poorer migratory aptitude. Bond length data are not available on the other complexes which are, in general, low melting waxes.

Selected spectral data of the new complexes are provided in Table I. All the infrared spectra of the migrated silyl group complexes exhibit two CO stretching bands, at higher frequencies than their parent $Fp–(Si)_n$ complexes, as expected from previous infrared studies on the Fp–C vs. Fp–Si complexes.[6]

A brief mention of the ^{29}Si NMR data is appropriate. Analysis of the chemical shift data is as previously reported,[11] i.e., δ(FpSi) − δ(MeSi) and δ(SiFpMe) − δ(SiMe), Δδ (Table II). Whereas Δδ for Si atoms attached directly to the coordination sphere of the metal via the metal atom are large and positive, +40 ppm, those attached directly via the cyclopentadienyl ligand are small and negative, −4 ppm. The β-Si atom shifts by approximately +11 ppm in the metal attached complexes but is almost unaffected, +0.5 ppm, in the SiFp–Me complexes. In both cases γ-silicon atoms are essentially unaffected by the coordination process as far as chemical shifts are concerned.

We have briefly studied the photochemical properties of the migrated polysilane complexes. There is no evidence for the deoligomerization process noted for the complexes where the silicon chain is directly bonded to the metal atom. Irradiation in the presence of PPh_3 yields the related phosphine-substituted monocarbonyl complexes with the silane chain intact.

Our results show that polysilane chains directly bonded to iron both readily depolymerize and migrate under different reaction conditions and that the depolymerization process is not observed in the migration products. Such chemistry may be of utility in the design of photoresist materials and their development and etching processes.

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Registry No. $Fp–SiMe_3$, 31811-63-9; $Fp–Si_2Me_5$, 53433-61-7; $Fp–SiMe_2SiMe_3$, 56784-37-3; $Fp–SiMe(SiMe_3)_2$, 53433-62-8; $Fp–SiMe_2SiPh_3$, 87882-62-0; $Fp–SiMe_2GePh_3$, 101247-90-9; $(MeC_5H_4)Fe(CO)_2–CH_2SiMe_2SiMe_3$, 101224-82-2; $Fp–SiPh_2Me$, 41619-97-0; $Fp–SiPhMe_2$, 41680-29-9; $Fp–SiPh_3$, 36835-55-9; $(Me_5Si_2C_5H_4)Fe(CO)_2–Me$, 101224-83-3; $Fp–CH_2SiMe_2SiMe_3$, 53695-99-1; $(Me_3SiC_5H_4)Fe(CO)_2CH_3$, 80611-30-9; $(Me_3SiMe_2SiMe_2SiC_5H_4)Fe(CO)_2CH_3$, 101224-84-4; $((Me_3Si)_2MeSiC_5H_4)Fe(CO)_2CH_3$, 101224-85-5; $(Ph_3SiMe_2SiC_5H_4)Fe(CO)_2CH_3$, 101224-86-6; $(Ph_3GeMe_2SiC_5H_4)Fe(CO)_2CH_3$, 101224-87-7.

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Activation of C–H Bonds by Rhenium. Catalytic Intermolecular H/D Exchange with $(\eta^6-C_6H_6)Re(PPh_3)_2H$

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Summary: The complex $(\eta^6-C_6H_6)Re(PPh_3)_2H$ is found to undergo slow photochemical loss of phosphine. The intermediate formed is capable of catalyzing H/D exchange between benzene-d_6 and other arenes in solution as well as with the meta and para hydrogens of the coordinated phosphine ligands. Labeling studies indicate that the simplest oxidative addition/reductive elimination mechanism is not operating in these exchanges.

Many new transition-metal complexes have been discovered during the past 3 years that are capable of activating the C–H bonds in hydrocarbons.[1-11] One class of

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