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Photochemical Transformations of Digermyl and Isomeric Silylgermyl and Germylsilyl Complexes of the (η^5-C_5H_5)Fe(CO)$_2$ System. Significant Stability of Germylene versus Silylene Intermediates[1]

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Summary: Photochemical treatment of the (digermyl)iron complex (η^5-C_5H_5)Fe(CO)$_2$GeMe$_2$GePh$_3$ (FpGeMe$_2$GePh$_3$) produced a mixture of FpGeMe$_2$Ph (10%), FpGeMePh$_2$ (82%), and FpGePh$_3$ (8%), a result that parallels the photochemistry of related Fp-disilyl complexes. Photochemical treatment of FpSiMe$_2$GeMe$_3$ yielded FpSiMe$_3$ (>95%) and traces of FpGeMe$_3$, whereas photochemical treatment of (η^5-C_5H_5)Fe(CO)$_2$SiMe$_2$GePh$_3$ yielded FpSiMePh$_2$ (66%), FpSiMe$_2$Ph (20%), and FpSiPh$_3$ (14%), i.e. no Fp-germyl complexes. The mechanism of these transformations parallels that reported for the related disilyl complexes, with the important distinction that intermediate silyl germylene complexes are more thermodynamically favored than the related germyl silylene intermediates. Photolysis of the isomeric (η^5-C_5H_5)Fe(CO)$_2$GeMe$_2$SiPh$_3$ produces the same Fp-silyl complexes, but in different yields, *plus* small amounts of the corresponding FpGeR$_3$ complexes, suggesting that complexes with direct Fe-Ge bonds possess another minor, and as yet unclear, pathway for photochemical degradation.

Investigations into the photochemistry of oligo- and polysilyl complexes of the (η^5-C_5H_5)Fe(CO)$_2$– (Fp) system have resulted in some remarkable, high-yield transformations (eqs 1–3).[2–6]

$$\left.\begin{array}{l}\mathrm{FpSiMe_2SiPh_3}\\ \mathrm{FpSiMePhSiPh_2Me}\end{array}\right] \longrightarrow \underset{8\%}{\mathrm{FpSiMe_2Ph}} + \underset{85\%}{\mathrm{FpSiMePh_2}} + \underset{7\%}{\mathrm{FpSiPh_3}} \qquad (1)$$

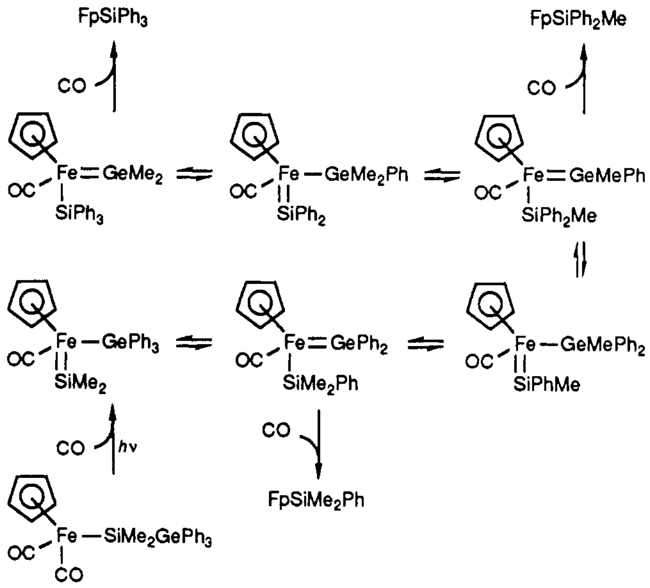
$$\mathrm{FpSiMe_2SiMe_2SiMe_2SiMe_3} \longrightarrow \mathrm{FpSi(SiMe_3)_3} \qquad (2)$$

$$\mathrm{FpSiMe_2SiMe_2Fp} \longrightarrow [(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)}]_2(\mu\text{-}\mathrm{CO})(\mu\text{-}\mathrm{SiMeSiMe_3}) \longrightarrow [(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)}]_2(\mu\text{-}\mathrm{SiMe_2})_2 \qquad (3)$$

We have extended these studies to germanium-containing complexes and wish to report the initial studies on the photochemistry of digermyl and isomeric silylgermyl and germylsilyl complexes of the Fp system. Synthesis of FpGeMe$_2$GePh$_3$ (I) was accomplished as shown in eq 4.[7]

$$\mathrm{FpGeMe_2Cl} + \mathrm{Ph_3GeLi} \rightarrow \underset{\mathrm{I}}{\mathrm{FpGeMe_2GePh_3}} + \mathrm{LiCl} \qquad (4)$$

Scheme I



Syntheses of the complexes FpSiMe$_2$GePh$_3$ (II), FpGeMe$_2$SiPh$_3$ (III), FpSiMe$_2$GeMe$_3$ (IV), and FpGeMe$_2$SiPh$_2$Me (V) were performed with use of either the published procedures (eq 5)[8] or that outlined in eq 6.[7]

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[7] Three typical synthetic procedures are outlined below. *Synthesis of FpGeMe$_2$GePh$_3$.* (Triphenylgermyl)lithium, prepared from 1.7 g (5.0 mmol) of Ph$_3$GeCl and 0.14 g (20.0 mmol) of lithium in 30 mL of THF, was added dropwise at −25 °C to a solution of 1.57 g (5.0 mmol) of FpGeMe$_2$Cl in 40 mL of THF. The solution was stirred, warmed to room temperature, and stirred for a further 12 h. Removal of solvents resulted in a brown-yellow gum, which was extracted with a hexane/methylene chloride mixture (40/60). After filtration and concentration to 5 mL, the resulting solution was placed upon a 2.5 × 15 cm silica gel column and eluted with a hexane/methylene chloride solvent mixture (80/20). Recovery of the yellow band developed upon elution with the same solvent mixture yielded 0.62 g (1.06 mmol, 21%) of yellow crystalline FpGeMe$_2$GePh$_3$, mp 126 °C. *Synthesis of FpGeMe$_2$SiPh$_3$.* (Triphenylsilyl)lithium, obtained from 1.47 g (5.0 mmol) of Ph$_3$SiCl and 0.14 g (20.0 mmol) of lithium metal in 30 mL of THF, was added dropwise to a THF solution of FpGeMe$_2$Cl (1.57 g, 5.0 mmol) at −25 °C. The system was warmed to room temperature, the reaction mixture was stirred for 10 h, and the solvent was removed. The reddish brown residue was extracted with 60 mL of a hexane/methylene chloride mixture (80/20). After filtration, the solution was concentrated to 5 mL and chromatographed through a silica gel column (2.5 × 20 cm). The initial yellow band was eluted with a hexane/methylene chloride mixture (80/20), and after removal of solvent, 0.5 g (0.92 mmol, 18%) of FpGeMe$_2$SiPh$_3$ was obtained as a yellow crystalline solid, mp 143 °C. *Synthesis of FpSiMe$_2$GeMe$_3$.* To a solution of [(η^5-C_5H_5)Fe(CO)$_2$]$^-$Na$^+$, prepared from 0.58 g (1.6 mmol) of [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ at −25 °C, was added 0.70 g (3.3 mmol) of Me$_3$GeSiMe$_2$Cl. The solution was stirred for 30 min, warmed to room temperature, and stirred for a further 10 h. The solvent was removed, and the resulting brown semisolid was extracted with 60 mL of hexane. The solution was filtered, and the concentrated filtrate (5 mL) was chromatographed through a silica gel column (2.0 × 20 cm). The yellow band was extracted with hexane. After removal of solvent, 0.30 g (0.85 mmol, 26%) of FpSiMe$_2$GeMe$_3$ was obtained as a yellow oil.

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Table I. Spectroscopic and Analytical Data for New Complexes[a]

	$FpGeMe_2SiPh_3$
% yield	18
anal. found (calcd)	C, 60.05, (60.15); H, 4.82 (4.90)
mp, °C	143
^1H NMR	0.60 ($GeMe_2$); 4.4 (η^5-C_5H_5); 7.36, 7.58 ($SiPh_3$)
^{13}C NMR	4.23 ($GeMe_2$); 82.85 (η^5-C_5H_5); 128.36, 129.49, 135.34, 136.49 (Ph_3Si); 216.23 (CO)
^{29}Si NMR	−11.69
IR ν(CO)	1996.3, 1947.6
	$FpGeMe_2GePh_3$
% yield	21
anal. found (calcd)	C, 55.32 (55.55); H, 4.54 (4.45)
mp, °C	123–125
^1H NMR	0.91 ($GeMe_2$); 3.99 (η^5-C_5H_5); 7.16, 7.72 ($GePh_3$)
^{13}C NMR	5.73 ($GeMe_2$); 82.93 (η^5-C_5H_5); 216.05 (CO)
IR ν(CO)	1998.4, 1949.7
	$FpGeMe_2SiPh_2Me$
% yield	16
anal. found (calcd)	C, 54.92 (55.39); H, 5.05 (5.03)
mp, °C	64–65
^1H NMR	0.75 ($GeMe_2$); 0.78 ($MePh_2$); 3.96 (η^5-C_5H_5); 7.16, 7.18, 7.64
^{13}C NMR	−2.25 ($GeMe_2$); 3.31 ($MePh_2$); 82.54 (η^5-C_5H_5); 127.66, 129.33, 135.23, 136.7 (Ph_2Me); 216.5 (CO)
^{29}Si NMR	−11.68
IR ν(CO)	1994.9, 1945.5
	$FpSiMe_2GeMe_3$
% yield	26
anal. found (calcd)	C, 41.09 (40.86); H, 6.23 (5.67)
mp, °C	oil
^1H NMR	0.31 ($GeMe_3$); 0.54 ($SiMe_2$); 4.15 (η^5-C_5H_5)
^{13}C NMR	−0.88 ($GeMe_3$); 4.25 ($SiMe_2$); 83.27 (η^5-C_5H_5); 215.33 (CO)
^{29}Si NMR	25.81
IR ν(CO)	1999.1, 1948.0

[a] NMR spectra (ppm) were recorded in C_6D_6 and IR spectra (cm^{-1}) were recorded in *n*-hexane.

Spectral and analytical data for all complexes are in accord with proposed structures and are presented in Table I.

$$Fp^-Na^+ + Ph_3GeSiMe_2Cl \rightarrow FpSiMe_2GePh_3 + NaCl \quad (5)$$

$$FpGeMe_2Cl + Ph_3Si^-Li^+ \rightarrow FpGeMe_2SiPh_3 + NaCl \quad (6)$$

Photolysis of I in C_6D_6 led to the formation of the three expected compounds, identified by spectral and HPLC comparison with independently synthesized, and fully characterized, samples (eq 7).[9] The relative amounts of the isomers formed are remarkably similar to those obtained upon photolysis of $FpSiMe_2SiPh_3$ (eq 1), presumably via a directly analogous reaction mechanism.

$$FpGeMe_2GePh_3 \rightarrow \underset{10\%}{FpGeMe_2Ph} + \underset{82\%}{FpGeMePh_2} + \underset{8\%}{FpGePh_3} \quad (7)$$

Photolysis of the (trimethylgermyl)dimethylsilyl Fp complex IV, or the isomeric $FpGeMe_2SiMe_3$, resulted in formation of $FpSiMe_3$ (>95%) and a small amount of $FpGeMe_3$ (<5%) as the resulting iron complexes. Photochemical treatment of complex II (C_6D_6 solutions in sealed NMR tubes, monitoring via ^{29}Si, ^{13}C, and ^1H NMR spectroscopy and reverse-phase HPLC) yielded only Fp–silane photoproducts (eq 6).

$$FpSiMe_2GePh_3 \rightarrow \underset{20\%}{FpSiMe_2Ph} + \underset{66\%}{FpSiMePh_2} + \underset{14\%}{FpSiPh_3} + \text{Ge polymer} \quad (8)$$

We suggest that the mechanism of this photoreaction is closely related to that of the Fp–oligosilane rearrangements and eliminations. Such a mechanism, outlined in Scheme I, involves entry into a rapidly established dynamic equilibrium of silyl germylene and germyl silylene intermediates followed by exclusive germylene expulsion upon recoordination of CO.

The system is not quite as simple as the disilyl system, where isomeric complexes yielded the same product distributions, since although photolysis of III yielded the same Fp–silane products, in different relative yields, it also produced related Fp–germane complexes, $FpGeR_3$, in low yields (10–15%). It is possible that some direct Fe–Ge cleavage is occurring upon photolysis of III, providing a radical route to monosilane and/or monogermane products; however, this is conjecture at the present stage of our study.

The results of this preliminary study show that the types of photoelimination reactions reported for Fp–disilanes also occur for Fp–digermanes and the mixed Fp–silylgermanes and –germylsilanes. For the mixed silicon/germanium complexes, product distributions show that dynamic equilibria involving methyl/phenyl 1,3-migrations are occurring at the stage of the germyl silylene and silyl germylene intermediates. The almost exclusive formation of the Fp–silyl complexes suggests that the equilibria favor the silyl germylene intermediates, from which recoordination of CO yields the $FpSiR_3$ complexes. Alternatively, equilibrium concentrations of the various intermediates are relatively similar, but the (η^5-C_5H_5)Fe(CO)(SiR_3)=GeR_2 species are more kinetically labile. Given the well-established stability of Ge(II) complexes, the former suggestion is more probable.[10]

Attempts to trap the R_2Si and/or R_2Ge fragments liberated during the photochemistry have not proven successful to date and are a major thrust of our current work. As yet in the case of the disilane chemistry, only various oligomeric siloxane materials have been isolated during various attempted trapping experiments.

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(9) The photolysis reactions were performed in two distinct manners, with use of concentrated solutions (0.37 M) in NMR tubes for direct ^{29}Si, ^{13}C, and ^1H NMR monitoring (with final HPLC monitoring) and also with use of dilute solutions (0.0037 M) for direct reverse-phase HPLC monitoring (Econosphere C-18, 5-μm packing, 70/30 CH_3CN/H_2O solvent mixture). Direct comparison of NMR resonances and retention times for the photoproducts and authentic, independently synthesized samples permitted accurate product analysis as noted in the text. For the Fp–disilane and Fp–digermane complexes the two sets of results were identical, whereas for the mixed Fp–silylgermane and Fp–germylsilane complexes variations in product distribution were obtained and are being investigated.

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