finement. The final $R$ factors were $R = 0.029$, $R_w = 0.040$, $p = 0.06$, and GOF = 1.02.

**Registry No.** 1, 131104-93-3; 2, 129117-81-3; 3, 131104-89-7; 4, 131104-92-2; 5, 141397-75-3; 6, 141397-76-4; 7, 141411-07-6; $Cr(bpy)(CO)_4$, 15668-63-0; $(PPh_3)_2CoCl_2$, 14126-40-0; $NiBr_2(DME)$, 28923-39-9; (4,4',5,5'-tetramethyl-2,2'-biphosphinine)tetracarbonylchromium, 131104-94-4.

**Supplementary Material Available:** X-ray structure determination for 1, including tables of crystal data, positional parameters, bond distances and angles for all non-hydrogen atoms, $\beta_{ij}$ values, least-squares planes, and torsion angles (7 pages). Ordering information is given on any current masthead page.

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# Photochemical Synthesis and Stereodynamic Behavior of Alkoxy-Bridged (Silylene)(germylene)iron Complexes

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Mixed (silylene)(germylene)iron complexes have been synthesized for the first time and are internally stabilized by a donor bridging alkoxy group: $[Cp'(CO)Fe\{GeMe_2\text{--}O(R)\text{--}SiMe_2\}]$ ($Cp' = C_5Me_5$; R = Me, $Bu^t$). Two-dimensional and variable-temperature $^1H$ NMR spectroscopies establish germylene–methyl group exchange. Computer simulation of the spectra and calculation using the Eyring equation yield values for $\Delta G^{\ddagger}_{298}$ for the process of 62 kJ $mol^{-1}$ (R = Me) and 61 kJ $mol^{-1}$ (R = $Bu^t$). A mechanism involving cleavage of the Ge--O partial bond, followed by rotation of the resulting coordinated germylene moiety about the Fe=Ge double bond, is proposed for this exchange. The (silylene)(germylene)iron complexes are weighted toward the (methoxysilyl)(germylene) form, indicating that germylene ligands are more stable than their silicon analogues.

## Introduction

Silylenes, well-known as reactive intermediates from their reactions with various trapping agents such as 1,3-butadiene and trimethylsilane,[1] remain, as yet, elusive, though their coordination chemistry is an area of stimulating and imaginative research. A number of unstable silylene complexes have been proposed as the intermediates of various reactions. Photochemical rearrangement of (disilanyl)carbonyliron complexes such as $CpFe(CO)_2SiMe_2SiMe_3$ ($Cp = C_5H_5$) reported by Pannell[2] and us[3] is one of the most well-defined reactions generating silylene-coordinated intermediates. Donor-stabilized silylene-metal complexes have been synthesized,[4-9] and more recently, reports have come describing cationic donor-free silylene complexes.[10] Another recently reported complex is a fluxional gold complex which has been described in terms of a coordinated silylene.[11] Germylene complexes are somewhat more stable, and there are consequently more reports concerning the synthesis and characterization of both base-stabilized[12] and base-free[12-14] species, including recently a paper describing exchange of moieties on a germyl group in a rhenium complex, probably via dissociation of a triflate group from the germyl group and rotation of the resulting germylene about the rhenium–germanium double bond.[15] Pannell recently reported the photolysis of (silylgermyl)- and (germylsilyl)iron complexes generating an equilibrium mixture of (silyl)(germylene) and (germyl)(silylene) intermediates and estimated the relative stability between silylene complexes and germylene com-

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plexes.[16] This is so far the only report on the direct comparison of the stability between silylene and germylene ligands.

Our work has covered internally base-stabilized bis(silylene) complexes[7] and more recently a comparison with analogous bis(germylene) complexes.[17] In order to further our comparative study of the effects of the different group 14 elements and the relative stabilities of coordinated silylenes and germylenes, we have synthesized and now report our investigations into mixed (silylene)(germylene) complexes and their dynamic stereochemistry and propose a mechanism for the observed germanium–methyl group exchange.

## Experimental Section

**Materials and Methods.** All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled from sodium benzophenone ketyl under nitrogen prior to use. Photolysis solvent $C_6D_5CD_3$ was dried with a potassium mirror. Na[FeCp′(CO)$_2$][18] (Cp′ = $C_5Me_5$) and $GeMe_2PhCl$[19] were prepared according to literature methods, and $SiHMe_2Cl$ was used as commercially obtained.

Infrared spectra were recorded using a JASCO IR-810 spectrometer. Mass spectra and high-resolution mass spectra were recorded using Hitachi M-52 and JEOL JMS-D300 spectrometers, respectively. $^1$H NMR spectra were recorded on a continuous-wave Varian EM-390 spectrometer operating at 90 MHz for monitoring photolysis and on a Bruker AM-600 at 600.139 MHz for two-dimensional and variable-temperature measurements. $^{29}$Si NMR spectra were recorded using a JEOL FX-90Q, operating at 17.75 MHz, and $^{13}$C NMR spectra using a Bruker AM-300 at 75.469 MHz.

**$ClGeMe_2SiMe_2Cl$.** A dark green solution of $GeMe_2PhLi$, prepared from $GeMe_2PhCl$ (13.50 g, 63 mmol) and finely chopped lithium wire (1.31 g, 188 mmol) in THF (60 cm$^3$), was added slowly to a cold solution of $SiHMe_2Cl$ (5.93 g, 63 mmol) in THF (40 cm$^3$) while stirring vigorously. After addition was complete, the solution was allowed to warm to room temperature and was stirred for a further hour. Water was then added and the product extracted with diethyl ether, dried over $MgSO_4$, and distilled (95 °C, 18 Torr) to yield $PhGeMe_2SiMe_2H$ (12.20 g, 51 mmol, 81%). IR (neat): $\nu$(SiH) 2098 cm$^{-1}$.

This product, $PhGeMe_2SiMe_2H$ (12.20 g, 50 mmol), was dissolved in benzene (35 cm$^3$) containing a catalytic amount of freshly sublimed $AlCl_3$, and dry HCl gas was bubbled through the solution. The reaction was monitored by GC and showed complete conversion after about 1 h. $ClGeMe_2SiMe_2H$ was distilled at 58 °C, 38 Torr (8.6 g, 44 mmol, 88%). IR (neat): $\nu$(Si–H) 2120 cm$^{-1}$.

Crude $ClGeMe_2SiMe_2H$ (5.0 g, 25 mmol) was mixed with $CCl_4$ (35 cm$^3$), and a catalytic amount of benzoyl peroxide was added to it. The mixture was heated to reflux with stirring and monitored by GC. The reaction was complete in about 30 min, after which the solvent was removed by distillation. $ClGeMe_2SiMe_2Cl$ (5.11 g, 22 mmol, 88%) was obtained as a clear liquid upon distillation (68 °C, 20 Torr). $^1$H NMR ($C_6D_6$): $\delta$ 0.40 (6 H, s, $SiMe_2$), 0.58 (6 H, s, $GeMe_2$). $^{13}$C NMR ($C_6D_6$): $\delta$ 2.0 ($SiMe_2$), 3.0 ($GeMe_2$). $^{29}$Si NMR ($C_6D_6$): $\delta$ 24.1.

**[Cp′(CO)$_2$FeGeMe$_2$SiMe$_2$Cl] (1).** To a stirring solution of $ClGeMe_2SiMe_2Cl$ (1.50 g, 6.47 mmol) in THF (25 cm$^3$) at −5 °C (salt and ice bath) was added dropwise a solution of Na[Fp′] (Fp′ is FeCp′(CO)$_2$) (6.47 mmol) in THF (50 cm$^3$). After addition was complete, the solution was allowed to warm to room temperature and then stirred at room temperature for 12 h. The solvent was then removed under reduced pressure and the product extracted with hexane. Purification of this by Kugelrohr molecular distillation (100 °C, 0.05 Torr) afforded [Cp′(CO)$_2$FeGeMe$_2$SiMe$_2$Cl] (1.37 g, 48%) as waxy orange crystals. $^1$H NMR ($C_6D_6$): $\delta$ 0.86 (6 H, s, $SiMe_2$), 0.90 (6 H, s, $GeMe_2$), 1.70 (15 H, s, Cp′). $^{13}$C NMR ($C_6D_6$): $\delta$ 1.2 ($SiMe_2$), 1.4 ($GeMe_2$), 10.0 ($C_5\mathit{Me}_5$), 94.8 ($\mathit{C}_5Me_5$), 217.8 (CO). $^{29}$Si NMR ($C_6D_6$): $\delta$ 32.6. IR (neat): $\nu$(CO) 1918 (vs), 1965 (vs) cm$^{-1}$. MS (25 eV): *m/z* 444 (M$^+$, 4.3), 351 (100). Anal. Calcd for $C_{16}H_{27}ClFeGe_2O_2$ (mol wt 443.4): C, 43.34; H, 6.14. Found: C, 43.18; H, 6.01.

**[Cp′(CO)$_2$FeGeMe$_2$SiMe$_2$OMe] (2).** Solid [Fp′GeMe$_2$SiMe$_2$Cl] (0.50 g, 1.10 mmol) was added to a solution of methanol (20 cm$^3$) and pyridine (0.4 cm$^3$), and the mixture was stirred for 2 h. The solvent was then removed under reduced pressure and the product extracted with hexane, the washings from which were filtered through a Celite pad to remove precipitated pyridinium hydrochloride. After molecular distillation (100 °C, 0.05 Torr), [Cp′(CO)$_2$FeGeMe$_2$SiMe$_2$OMe] (0.35 g, 71%) was obtained as low-melting waxy orange crystals. $^1$H NMR ($C_6D_6$): $\delta$ 0.50 (6 H, s, $SiMe_2$), 0.75 (6 H, s, $GeMe_2$), 1.68 (15 H, s, Cp′), 3.40 (3 H, s, OMe). $^{13}$C NMR ($C_6D_6$): $\delta$ 0.3 ($SiMe_2$), 1.6 ($GeMe_2$), 10.0 ($C_5\mathit{Me}_5$), 50.3 (OMe), 94.5 (*C5*Me$_5$), 218.2 (CO). $^{29}$Si NMR ($C_6D_6$): $\delta$ 20.9. IR (neat): $\nu$(CO) 1925 (vs), 1976 (vs) cm$^{-1}$. MS (70 eV): *m/z* 440 (M$^+$, 3.07), 351 (100). Anal. Calcd for $C_{17}H_{30}FeGeO_3Si$ (mol wt 438.95): C, 46.52; H, 6.89. Found: C, 46.28; H, 6.66.

**[Cp′(CO)$_2$FeGeMe$_2$SiMe$_2$OBu$^t$] (3).** This was obtained similarly to the methoxy derivative except that the alkoxylation conditions employed excess (3 equiv) potassium *tert*-butoxide in THF (20 cm$^3$). $^1$H NMR ($C_6D_5CD_3$): $\delta$ 0.70 (6 H, s, $SiMe_2$), 0.82 (6 H, s, $GeMe_2$), 1.45 (9 H, s, OBu$^t$), 1.88 (15 H, s, Cp′). $^{13}$C NMR ($C_6D_5CD_3$): $\delta$ 1.7 (SiMe), 4.4 (GeMe), 10.3 ($C_5\mathit{Me}_5$), 32.4 ($C\mathit{Me}_3$), 73.8 ($\mathit{C}Me_3$), 94.5 ($\mathit{C}_5Me_5$), 218.4 (CO). $^{29}$Si NMR ($C_6D_5CD_3$): $\delta$ 13.9. IR (neat): $\nu$(CO) 1912 (vs), 1967 (vs) cm$^{-1}$. MS (70 eV): *m/z* 482 (M$^+$, 2.36), 351 (100). Anal. Calcd for $C_{20}H_{36}FeGeO_3Si$ (mol wt 481.03): C, 49.94; H, 7.54. Found: C, 49.41; H, 7.21.

**[Cp′(CO)Fe{GeMe$_2$--O(Me)--SiMe$_2$}] (4).** 4 was synthesized photochemically; see Photolysis of [Cp′(CO)$_2$FeGeMe$_2$SiMe$_2$OR] subsection. $^1$H NMR ($C_6D_5CD_3$): $\delta$ 0.49 (3 H, s, SiMe), 0.55 (3 H, s, SiMe), 0.74 (6 H, s, $GeMe_2$), 1.78 (15 H, s, Cp′), 2.76 (3 H, s, OMe). $^{13}$C NMR ($C_6D_5CD_3$): $\delta$ 5.7 (SiMe), 7.1 (SiMe), 9.8 (GeMe), 10.0 (GeMe), 11.7 ($C_5\mathit{Me}_5$), 50.0 (OMe), 89.4 ($\mathit{C}_5Me_5$), 220.8 (CO). $^{29}$Si NMR ($C_6D_5CD_3$): $\delta$ 114.3. IR (neat): $\nu$(CO) 1879 cm$^{-1}$. Exact Mass Calcd for $C_{16}H_{30}FeGeO_2Si$: 412.0576. Found: 412.0573.

**[Cp′(CO)Fe{GeMe$_2$--O(Bu$^t$)--SiMe$_2$}] (5).** 5 was synthesized photochemically; see Photolysis of [Cp′(CO)$_2$FeGeMe$_2$SiMe$_2$OR] subsection. $^1$H NMR ($C_6D_5CD_3$): $\delta$ 0.90 (3 H, s, SiMe), 0.95 (3 H, s, SiMe), 1.19 (6 H, s, $GeMe_2$), 1.28 (9 H, s, OBu$^t$), 2.00 (15 H, s, Cp′). $^{13}$C NMR ($C_6D_5CD_3$): $\delta$ 10.3 (SiMe), 11.4 ($C_5\mathit{Me}_5$), 11.7 (SiMe), 14.3 ($GeMe_2$), 31.2 ($C\mathit{Me}_3$), 82.6 ($\mathit{C}Me_3$), 89.1 ($\mathit{C}_5Me_5$), 220.1 (CO). $^{29}$Si NMR ($C_6D_5CD_3$): $\delta$ 110.4. IR (neat) $\nu$(CO) 1882 cm$^{-1}$. Exact Mass Calcd for $C_{19}H_{36}FeGeO_2Si$: 454.1046. Found: 454.1052.

**Photolysis of [Cp′(CO)$_2$FeGeMe$_2$SiMe$_2$OR] (R = Me, Bu$^t$).** The sample was placed in a thick-walled Pyrex NMR tube (o.d. 5 mm) and $C_6D_5CD_3$ transferred to it by vacuum line trap-to-trap techniques. The tube was sealed under vacuum, and the sample was irradiated in an ice–water bath using a medium-pressure mercury lamp placed in a water-cooled quartz jacket, for about 45 min, while periodically monitoring the course of the reaction by $^1$H NMR spectroscopy.

## Results and Discussion

**Synthesis of Photolysis Precursors.** Combination of (phenyldimethylgermyl)lithium with dimethylchlorosilane afforded a silylgermane, which, after 1,2-dichlorination and reaction with dicarbonyl(pentamethylcyclopentadienyl)ferrate, gave a single product, as evidenced by its $^1$H NMR spectrum, which was considered to be the germanium-bound complex, [Fp′GeMe$_2$SiMe$_2$Cl] (1), and none of the other possible, silicon-bound, geometrical isomers on the basis of the mass spectrum of the product in which fragments due to cleavage of the Ge–Si bond 1 were evident (the Fp′GeMe$_2$ fragment constitutes the base peak). There were no peaks which could be assignable to the silicon-bound isomer. Alkoxylation of the chloro complex gives the photolysis precursors, [Cp′-

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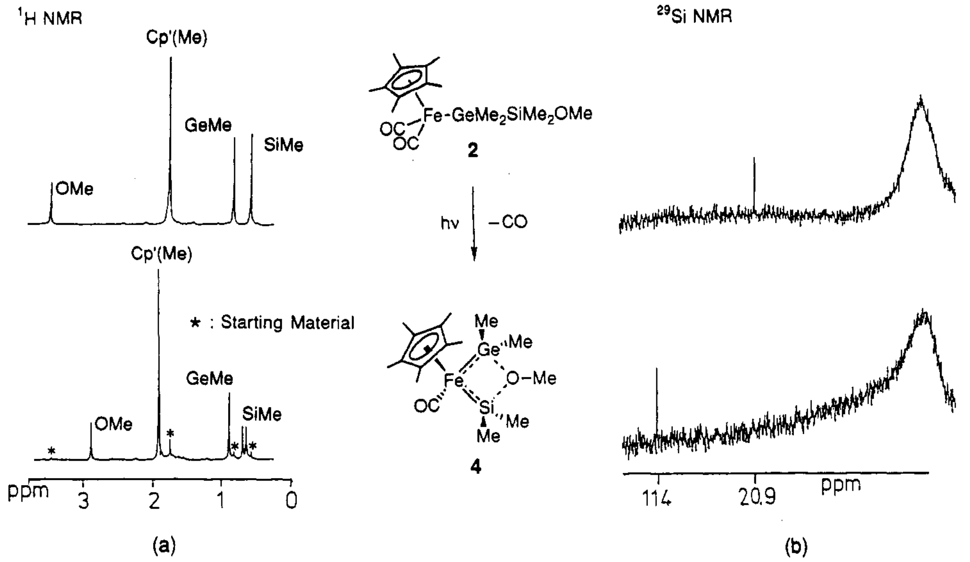
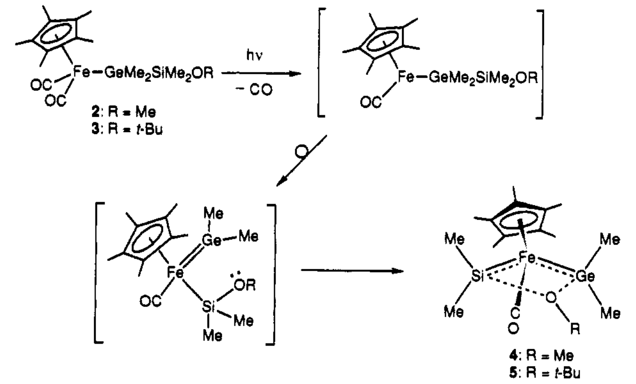
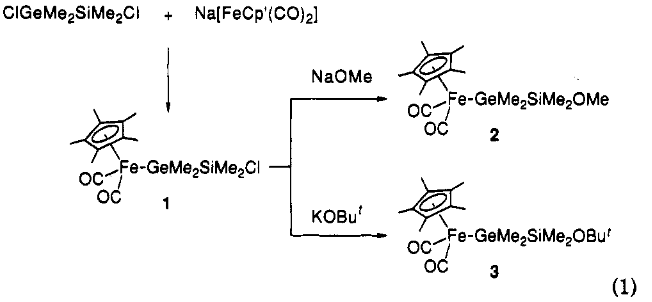


**Figure 1.** NMR spectroscopic change upon photolysis for Cp′Fe(CO)$_2$GeMe$_2$SiMe$_2$OMe (**2**): (a) $^1$H NMR (90 MHz), (b) $^{29}$Si NMR (17.75 MHz; the broad signal at high field is due to the glass of the NMR tube).

**Scheme I**



(CO)$_2$FeGeMe$_2$SiMe$_2$OR] (**2**, R = Me; **3**, R = Bu$^t$), as shown in eq 1. UV photolysis of these yields the extremely air- and moisture-sensitive alkoxy-bridged products.



(1)

**Photochemistry of [Fp′GeMe$_2$SiMe$_2$OR]. Formation of [Cp′(CO)Fe{GeMe$_2$--O(R)--SiMe$_2$}].** Photolysis of [Fp′GeMe$_2$SiMe$_2$OR] (**2**, R = Me; **3**, R = Bu$^t$) in C$_6$D$_5$CD$_3$ was monitored by $^1$H NMR spectroscopy (Figure 1a). A splitting of signals for the Si methyls and a broadening of a signal for the Ge methyls were observed (see below about the assignments of the signals). Photolysis was stopped after about 95% conversion, as some decomposition also occurred. In the case of the unsubstituted cyclopentadienyl complex, photolysis resulted in complete decomposition.

The $^{29}$Si NMR signal in the photolysis precursor [Fp′GeMe$_2$SiMe$_2$OR] appears slightly to low field of TMS. After photolysis, the $^{29}$Si signal of the products appears far to low field of TMS (Figure 1b). This is similar to the shift observed in the case of the photolysis of some alkoxy disilanyliron complexes, where the product was considered to be a bis(silylene) complex containing a bridging alkoxy group.[7] It is therefore considered that photolysis of the mixed silylgermyl complex leads to a similarly alkoxy-bridged (silylene)(germylene) species (Scheme I). The proposed reaction mechanism is closely related to the photoreaction mechanism for (silylgermyl)- and (germylsilyl)iron complexes reported by Pannell[16] and is also directly analogous to that of the formation of bis(silylene) complexes.[7]

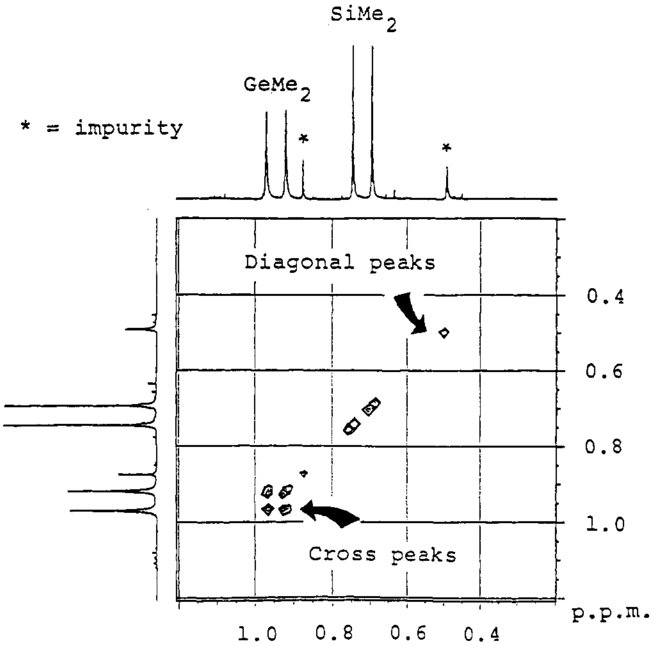


**Figure 2.** Two-dimensional EXSY $^1$H NMR spectrum of [Cp′(CO)Fe{GeMe$_2$--O(Me)--SiMe$_2$}] (**4**) recorded at 263 K with mixing time, $\tau_m$, of 1 s. Cross peaks identify chemical exchange between Ge–methyl groups.

The difference in the $^{29}$Si chemical shift between the methoxy(silylene)(germylene) complex **4** (114.3 ppm) and the methoxybis(silylene) complex Cp′Fe(CO){SiMe$_2$--O(Me)--SiMe$_2$} (125.2 ppm)[4b] may be a result of slightly greater sp$^3$ hybridization at silicon in the former, resulting from the greater bond strength of Si–O compared with Ge–O. This would indicate a greater weighting of the two canonical extremes of the complex toward the (germylene)(silyl)iron form, suggesting greater stability of ger-

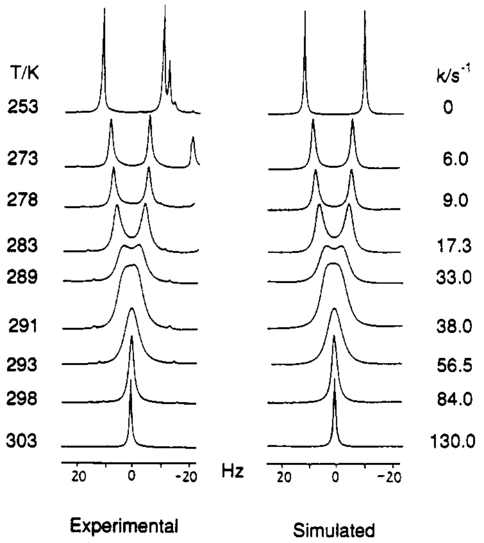


**Figure 3.** Experimental and computer-simulated variable-temperature $^1$H NMR spectra and rate constants, $k$, for germylene–methyl exchange in [Cp'(CO)Fe{GeMe$_2$--O(Me)--SiMe$_2$}] (4).

mylene compared to silylene.

**Two-Dimensional and Variable-Temperature $^1$H NMR and Stereodynamic Behavior.** After photolysis of 2, the room-temperature $^1$H NMR spectrum showed three peaks in the Si/Ge–methyl region: two sharp close signals and one broader, slightly downfield, signal (Figure 1a). At 600 MHz and by reducing the temperature to about 5 °C, two features became evident. Firstly, the single, broad signal had split into a broad doublet, and secondly, satellite peaks (5.5 Hz) were observed for the two sharp signals. This suggested that the two higher field sharp signals were due to Si–methyls with $^{29}$Si–$^1$H coupling and that the other two were due to two Ge–methyls, the environments of which were being interchanged at higher temperatures by a fluxional process. To confirm this, a two-dimensional EXSY[20] (exchange spectroscopy: phase-sensitive NOESY) spectrum was recorded. Figure 2 shows an example of such a spectrum obtained at −10 °C using the Bruker automation program NOESYPH, for which the mixing time, $\tau_m$, was 1 s. The spectrum clearly identifies the exchanging Ge–methyl groups by the presence of cross peaks[20] connecting the Ge–methyl signals; the absence of such cross peaks for the Si–methyl groups indicates that the Si–methyl groups do not exchange at this temperature on the NMR time scale. Full variable-temperature $^1$H NMR analyses at 600 MHz in $C_6D_5CD_3$ for both methoxy and *tert*-butoxy complexes substantiated this. At low temperature (−60 °C), the fluxional process occurs too slowly to be observed on the NMR time scale, but as the temperature is raised, the Ge–methyl peaks gradually broaden, coalesce at 291 K, and then become a sharp singlet at temperatures above 303 K, indicating fast exchange of the Ge–methyl groups.

Kinetic and thermodynamic parameters for the fluxional process were quantitatively evaluated by computer simulation of these spectra using the program DNMR3[21] and visual fitting to the experimental spectra (Figure 3). This gave values of the exchange rate, $k$, for which Eyring plots of ln ($k/T$) *vs* $1/T$ (Figure 4) afforded the enthalpy, entropy, and Gibbs' free-energy terms, $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta G^\ddagger_{298}$, respectively (see Table I).

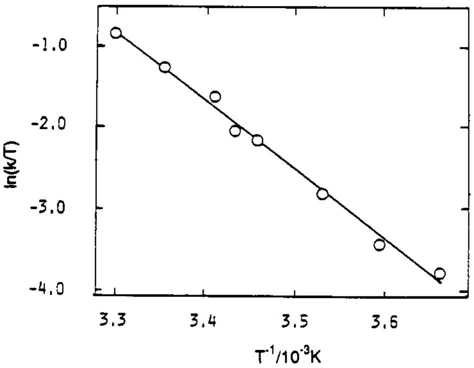


**Figure 4.** Eyring plot of ln ($k/T$) vs $1/T$ for [Cp'(CO)Fe{GeMe$_2$--O(Me)--SiMe$_2$}] (4).

**Table I. Thermodynamic Parameters for Germylene Rotation in [Cp'(CO)Fe{GeMe$_2$--O(R)--SiMe$_2$}] (4, R = Me; 5, R = Bu$^t$) and Comparison with [Cp'(CO)Fe{GeMe$_2$--O(Me)--GeMe$_2$}] (6)**

| complex | $\Delta H^\ddagger$/kJ mol$^{-1}$ | $\Delta S^\ddagger$/J K$^{-1}$ mol$^{-1}$ | $\Delta G^\ddagger_{298}$/kJ mol$^{-1}$ |
|---|---|---|---|
| 4 | 70.5 ± 2.0 | 28.5 ± 7.0 | 62.0 ± 4.1 |
| 5 | 95.8 ± 2.5 | 117.7 ± 8.7 | 61.0 ± 5.1 |
| 6[a] | 95.3 ± 2.6 | 27.1 ± 6.2 | 87.2 ± 4.4 |

[a] From ref 17, recalculated for rotation of one germylene moiety only.

**Mechanism of Exchange.** It is reasonable to assume that the mechanism of the Ge–methyl exchange for (silylene)(germylene) complexes is essentially the same as that for the bis(germylene) complex which we reported previously.[17] Thus, the mechanism involves cleavage of a Ge--O partial bond, followed by rotation of the resulting coordinated germylene moiety about the Fe=Ge double bond to interchange the methyl group environments. A similar rotation of a carbene group has been studied both experimentally, in the case of [Cp(Ph$_2$PCH$_2$CH$_2$PPh$_2$)-Fe=CH$_2$]$^+$ ($\Delta G^\ddagger$ for carbene rotation: 43.5 ± 4.2 kJ mol$^{-1}$),[22] and theoretically for [Cp(CO)$_2$Fe=CH$_2$]$^+$ ($\Delta G^\ddagger$ for carbene rotation: 26.04 kJ mol$^{-1}$).[23] Finally, recombination of the Ge--O partial bond regenerates the alkoxy-bridged species.

$\Delta S^\ddagger$ for the germanium–methyl exchange process is small, consistent with an intramolecular mechanism. For the *tert*-butoxy complex, $\Delta S^\ddagger$ is slightly greater than for the methoxy complex. This is likely to be a reflection of the greater degree of freedom and number of ways to dissipate energy in the *tert*-butoxy transition state than in that of the methoxy complex. The enthalpy change for the *tert*-butoxy complex is also greater, reflecting the increased Ge--OR bond strength due to the increased electron donation when R is *tert*-butoxy compared to methyl. These increases in both $T\Delta S^\ddagger$ and $\Delta H^\ddagger$ for the *tert*-butoxy complex are virtually equivalent, resulting in approximately equal values of $\Delta G^\ddagger_{298}$ for both methoxy and *tert*-butoxy complexes (62 and 61 kJ mol$^{-1}$, respectively). It should be noted that $\Delta G^\ddagger$ represents the free-energy difference between the metallacyclic ground state and the germylene complex transition state (GeMe$_2$ moiety rotated so as to be coplanar with Fe and Si atoms). It is not possible to separate the energy terms for the two steps, Ge--O bond cleavage and germylene rotation, in the mechanism, but based on the rotational energy barriers for the carbene complexes (vide supra), a not insubstantial

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contribution to the overall energy barrier by the germylene rotation step is likely. Gladysz[15] discusses a very similar situation concerning the equilibria involving the germylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}GePh_2)]^+TfO^-$: $\Delta G^{\ddagger}_{268} = 52.7$ kJ mol$^{-1}$ for the exchange of the diastereotopic germyl phenyl groups in this complex, ascertained by coalescence studies of the variable-temperature $^{13}C$ NMR spectra, and is described in terms of both triflate dissociation and germylene rotation, a separation of these terms being similarly impossible.

We previously reported a dynamic NMR study of a similar fluxional process occurring in a bis(germylene)iron complex, $[Cp'(CO)Fe\{GeMe_2\text{--}O(Me)\text{--}GeMe_2\}]$, where both germylene moieties are considered to rotate.[17] In that paper, the thermodynamic parameters were evaluated for a fluxional cycle comprising rotation of both germylene moieties. Recalculation of these for rotation of only one germylene allows a better comparison of the energies with those of the (silylene)(germylene) complexes. It is clear that while $\Delta S^{\ddagger}$ for the bis(germylene) complex (27 J K$^{-1}$ mol$^{-1}$) is virtually equivalent to that for the methoxy(silylene)(germylene) complex (see Table I), due to the virtually equivalent degrees of freedom in the transition states, both $\Delta H^{\ddagger}$ (95 kJ mol$^{-1}$) and $\Delta G^{\ddagger}_{298}$ (87 kJ mol$^{-1}$) are much greater. This is consistent with the proposed structures for the two complexes: The bis(germylene) complex has equivalent Ge--O bonds, whereas the (silylene)(germylene) complex is considered to be weighted toward a methoxy(silyl)(germylene) complex, strengthening the Si–O bond at the expense of the Ge–O bond. This is due to stronger Si–O bonding compared with Ge–O bonding and also indicates greater stability of the germylene ligand compared to the silylene ligand. It should be noted that the same conclusion as the latter has been drawn by Pannell from the extensive study on the photolysis of (silylgermyl)- and (germylsilyl)iron complexes, $CpFe(CO)_2GeMe_2SiR_3$ and $CpFe(CO)_2SiMe_2GeR_3$ (R = Me, Ph).[16] These reactions almost exclusively afforded monosilyl complexes $CpFeSiMe_nR_{3-n}$, and the formation of $CpFeGeMe_nR_{3-n}$ was negligible. These observations were reasonably explained on the assumption that the equilibria between (silyl)(germylene) and (germyl)(silylene) intermediates favor the former, from which recombination of CO yields the $CpFe(CO)_2SiMe_nR_{3-n}$ complexes.

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# Syntheses of Methylcyclopentadienyl Derivatives of Lanthanides (Ln = La–Nd) and Crystal Structures of $[(THF)_2Li(\mu\text{-}Cl)_2]_2[MeCpNd(THF)]$ and $[Li(DME)_3][MeCpLa(NPh_2)_3]$

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The reaction of $LnCl_3{\cdot}2LiCl$ with 1 equiv of MeCpNa in THF gives the complexes $[(THF)_2Li(\mu\text{-}Cl)_2]_2[MeCpLn(THF)]$ (Ln = Nd (**1**), La (**2**)) in good yield. These precursors react further with 2 equiv of $LiNPh_2$ to produce the new complexes $[Li(DME)_3][MeCpLn(NPh_2)_3]$ (Ln = La (**3**), Pr (**4**), Nd (**5**)). They have been characterized by elemental analyses and IR and NMR spectra, as well as by structural analyses of **1** and **3**. The chloride **1** crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with $a = 12.130$ (5) Å, $b = 17.343$ (5) Å, $c = 17.016$ (5) Å, $\beta = 108.54$ (3)°, $V = 3393.87$ Å$^3$, $Z = 4$, and $D_c = 1.45$ g/cm$^3$. Least-squares refinement led to a final $R$ value of 0.051 ($I \geqslant 3\sigma(I_o)$) for 2004 independent reflections. Complex **3** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 18.335$ (6) Å, $b = 16.576$ (5) Å, $c = 17.461$ (6) Å, $\beta = 96.04$ (3)°, $V = 5277.17$ Å$^3$, $D_c = 1.26$ g/cm$^3$, $Z = 4$, and $R = 0.057$ ($I \geq 2.5\sigma(I_o)$) for 3378 reflections. The structure of **3** consists of discrete ion pairs $[Li(DME)_3]^+$ and $[MeCpLa(NPh_2)_3]^-$ with average La–N and La–C(ring) distances of 2.459 (8) and 2.84 (1) Å, respectively.

## Introduction

Organolanthanide chemistry has undergone rapid growth in recent years. However, much of the work has been concentrated on the smaller and later lanthanide elements. Because of the lanthanide constriction effect and coordinative unsaturation, the important precursor lanthanide cyclopentadienyl and smaller substituted cyclopentadienyl chlorides of the early lanthanides have not been easily synthesized. Now it has been found that some approaches can be used to prepare such kinds of complexes for early lanthanides. These include the use of bulkier ligands such as $C_5Me_5$,[1,2] $C_5Me_4C_3H_7$,[3] $(Me_3Si)_2Cp$,[4] $^tBuCp$,[5]

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