

Synthesis and Rearrangements of Tungsten Germyl Silyl Complexes

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Germyl silyl complexes $\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{GeR}_3)$ have been synthesized by the reaction of the tungsten silene complex $\text{Cp}_2\text{W}(\eta^2\text{-Me}_2\text{Si}=\text{CH}_2)$ with germanes HGeR_3 ($\text{GeR}_3 = \text{GeMe}_3$ (**2**), GeMe_2H (**3a**), $\text{Ge}^t\text{Bu}_2\text{H}$ (**3b**), GePh_2H (**3c**)). Chlorogermyl derivatives are synthesized by the reaction of **3a-c** with CCl_4 to yield $\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{GeMe}_2\text{Cl})$ (**4a**), $\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{Ge}^t\text{Bu}_2\text{Cl})$ (**4b**), and $\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{GePh}_2\text{Cl})$ (**4c**). Complex **4a** has been structurally characterized by a single-crystal X-ray diffraction study. The corresponding triflate derivative, $\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{GeMe}_2\text{OTf})$ (**5a**), has been prepared by the reaction of **4a** and trimethylsilyl triflate. Substitution of triflate for chloride in $\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{Ge}^t\text{Bu}_2\text{Cl})$ (**4b**) requires mild heating (80°C) and is accompanied by concurrent redistribution of groups between silyl and germyl centers to yield the silyl triflate $\text{Cp}_2\text{W}(\text{SiMe}_2\text{OTf})(\text{Ge}^t\text{Bu}_2\text{Me})$ (**6b**). Under thermolytic conditions, germyl silyl complexes undergo intra- and intermolecular redistribution of substituents between the germyl and silyl ligands. This process is proposed to occur via a cationic germylene complex formed by triflate or chloride dissociation.

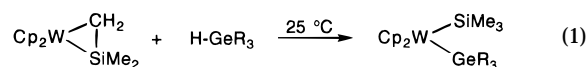
Introduction

Although stable germylene complexes have been known for many years,² it is only very recently that base-free silylene complexes have been isolated³ and structurally characterized.⁴ Germylene and silylene complexes are of particular interest because of their apparent involvement as intermediates in a wide variety of catalytic and stoichiometric reaction mechanisms ranging from dehydrogenative coupling to redistribution of silanes and germanes. Over the last several years, there has been mounting evidence that the redistribution of alkyl groups between silicon centers requires the intermediacy of an electrophilic silylene complex.⁵ In particular, the Pannell and Ogino groups have explored a variety of photochemically induced⁶ redistribution and alkyl scrambling processes in oligo silyl metal complexes and provided both indirect^{5a-e} and structural^{5h,i} evidence for silylene intermediates. These workers have also recently investigated mixed silyl germyl systems and

observed similar results.⁷ Our group has described the migration of alkyl groups between silicon centers in a series of tungsten bis(silyl) complexes, $\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{SiR}_2\text{X})$,⁸ and provided evidence that cationic silylene intermediates, in this instance formed by anion dissociation, are also key to the redistribution process. In this report we describe the synthesis of a related series of functionalized tungsten germyl silyl complexes of the formula $\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{GeR}_2\text{X})$, and report the intra- and intermolecular rearrangements which are observed.

Results

Synthesis. We have recently reported the facile reaction of the tungstenocene silene complex $\text{Cp}_2\text{W}(\eta^2\text{-SiMe}_2=\text{CH}_2)$ with various silanes to yield a series of bis(silyl) compounds.⁹ The analogous reaction of $\text{Cp}_2\text{W}(\eta^2\text{-SiMe}_2=\text{CH}_2)$ with a variety of germanes cleanly yields the tungstenocene germyl silyl complexes $\text{Cp}_2\text{W}(\text{GeR}_3)(\text{SiMe}_3)$ ($\text{GeR}_3 = \text{GeMe}_3$ (**2**), GeMe_2H (**3a**), $\text{Ge}^t\text{Bu}_2\text{H}$ (**3b**), GePh_2H (**3c**)) as shown in eq 1.



	GeR_3	% yield
2	GeMe_3	62
3a	GeMe_2H	71
3b	$\text{Ge}^t\text{Bu}_2\text{H}$	65
3c	GePh_2H	80

The reactions are complete after 1–5 days at 25°C depending on the germane, with more sterically de-

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Table 1. ^1H , ^{13}C and ^{29}Si NMR Data (δ , ppm; J , Hz) for Tungsten Germyl Silyl Complexes

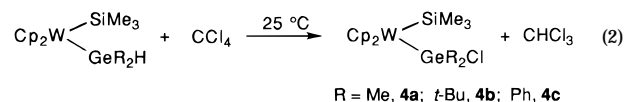
compd	^1H	$^{13}\text{C}\{^1\text{H}\}$	^{29}Si
$\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{GeMe}_3)$ (2)	3.86 (s, 10H, Cp) 0.46 (s, 9H, GeMe ₃)	77.16 (Cp) 9.25 (GeMe ₃)	2.1 ($J_{\text{W-Si}} = 90$)
$\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{GeMe}_2\text{H})$ (3a)	0.38 (s, 9H, SiMe ₃) 4.10 (sept, $^3J_{\text{H-H}} = 3.5$, 1H SiH) 3.84 (s, 10H, Cp) 0.55 (d, $^3J_{\text{H-H}} = 3.5$, 6H, GeMe ₂)	7.69 (SiMe ₃) 77.11 (Cp) 7.72 (GeMe ₂) 2.16 (SiMe ₃)	1.3 ($J_{\text{W-Si}} = 94$)
$\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{Ge}^t\text{Bu}_2\text{H})$ (3b)	0.41 (s, 9H, SiMe ₃) 4.06 (s, 10H, Cp) 3.80 (s, 1H, GeH) 1.28 (s, 18H, ^t Bu)	77.38 (Cp) 34.45 (CMe ₃) 31.68 (CMe ₃)	-0.6 ($J_{\text{W-Si}} = 107$)
$\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{GePh}_2\text{H})$ (3c)	0.51 (s, 9H, SiMe ₃) 7.66 (m, 4H, <i>o</i> -C ₆ H ₅) 7.21 (m, 4H, <i>m</i> -C ₆ H ₅) 7.13 (m, 2H, <i>p</i> -C ₆ H ₅) 5.49 (s, 1H, Ge-H) 3.89 (s, 10H, Cp)	10.04 (SiMe ₃) 148.6 (<i>i</i> -C ₆ H ₅) 135.9 (<i>o</i> -C ₆ H ₅) 127.7 (<i>m</i> -C ₆ H ₅) 127.1 (<i>p</i> -C ₆ H ₅) 78.1 (Cp)	1.6 ($J_{\text{W-Si}} = 90$)
$\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{GeMe}_2\text{Cl})$ (4a)	0.44 (s, 9H, SiMe ₃) 4.05 (s, 10H, Cp) 1.05 (s, 6H, GeMe ₂) 0.21 (s, 9H, SiMe ₃)	7.5 (SiMe ₃) 79.85 (Cp) 13.49 (GeMe ₂) 9.09 (SiMe ₃)	2.7 ($J_{\text{W-Si}} = 95$)
$\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{Ge}^t\text{Bu}_2\text{Cl})$ (4b)	4.16 (s, 10H, Cp) 1.29 (s, 18H, ^t Bu) 0.53 (s, 9H, SiMe ₃)	78.72 (Cp) 39.66 (CMe ₃) 32.69 (CMe ₃) 10.44 (SiMe ₃)	-1.5 ($J_{\text{W-Si}} = 103$)
$\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{GePh}_2\text{Cl})$ (4c)	7.81 (m, 4H, <i>o</i> -C ₆ H ₅) 7.21 (m, 4H, <i>m</i> -C ₆ H ₅) 7.10 (m, 2H, <i>p</i> -C ₆ H ₅) 4.04 (s, 10H, Cp) 0.43 (s, 9H, SiMe ₃)	150.4 (<i>i</i> -C ₆ H ₅) 134.6 (<i>o</i> -C ₆ H ₅) 128.0 (<i>m</i> -C ₆ H ₅) 127.7 (<i>p</i> -C ₆ H ₅) 80.1 (Cp) 9.0 (SiMe ₃)	3.5 ($J_{\text{W-Si}} = 90$)
$\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{GeMe}_2\text{OTf})$ (5a)	4.16 (s, 10H, Cp) 0.91 (s, 6H, GeMe ₂) 0.03 (s, 9H, SiMe ₃)	80.45 (Cp) 14.14 (GeMe ₂) 9.12 (SiMe ₃)	2.4 ($J_{\text{W-Si}} = 88$)
$\text{Cp}_2\text{W}(\text{SiMe}_2\text{OTf})(\text{Ge}^t\text{Bu}_2\text{Me})$ (6b)	4.23 (s, 10H, Cp) 0.95 (s, 18H, ^t Bu) 0.89 (s, 3H, GeMe) 0.05 (s, 6H, SiMe ₂)	78.63 (Cp) 32.83 (CMe ₃) 32.34 (CMe ₃) 11.25 (GeMe) 0.07 (SiMe ₂)	113.6 ($J_{\text{W-Si}} = 154$)
$[\text{Cp}_2\text{W}(\mu-\eta^5, \eta^1\text{-C}_5\text{H}_4\text{GeMe}_2)(\mu\text{-GeMe})\text{W}(\text{Cp})(\text{H})]^+[\text{OTf}]^-$ (7)	4.91 (s, 5H, Cp) 4.75 (s, 5H, Cp) 4.59 (s, 5H, Cp) 1.73 (s, 3H, GeMe) 0.48 (s, 3H, GeMe ₂) 0.44 (s, 3H, GeMe ₂) 5.88 (m, 1H, Cp-Ge) 5.30 (m, 1H, Cp-Ge) 5.17 (m, 1H, Cp-Ge) -10.80 (s, 1H, W-H)		

manding germanes requiring the longer times. Yields of isolated products range from 62 to 80%. NMR data for all compounds is listed in Table 1.

Given the known facile redistribution of groups in the tungstenocene bis(silyl) complexes, it is important to clearly establish the nature of the groups on the germyl and silyl ligands. Assignment of **2** is unambiguous; each center has three methyl groups, and each exhibits a singlet in the ^1H NMR. It is more difficult to conclusively distinguish $-\text{GeMe}_2\text{H}$ and $-\text{SiMe}_2\text{H}$ groups; however, the structure of **3a** is indicated by the trends in chemical shifts (^1H and ^{29}Si) and by the regiochemistry of the chlorination product (vide infra). The Ge-H/Si-H ambiguity does not exist for the *tert*-butyl or phenyl complexes **3b,c**, in which the $\text{GeR}_2\text{-H}$ hydride resonance is a singlet, whereas an SiMe_2H hydride resonance would be coupled to the methyl groups.

Although chlorosilyl derivatives, $\text{Cp}_2\text{W}(\text{SiR}_2\text{Cl})(\text{SiMe}_3)$, can be synthesized by the reaction of the tungsten silene complex **1** with silanes of the formula HR_2SiCl ,⁹ analogous germane starting materials are not commercially available. Fortunately, the Ge-H bond in **3a-c** can be

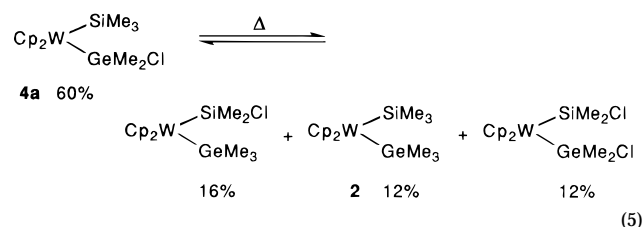
clearly converted to Ge-Cl bonds upon reaction with CCl_4 as shown in eq 2.



The ^1H NMR spectra of **4a-c** are very similar to **3a-c** with the exception of the absence of the Ge-H resonance and a significant downfield shift of the methyl groups on germanium in **4a**. It is clear that the chlorination of the Ge-H occurs without redistribution from the ^{29}Si NMR spectra of **4a**, which exhibits a resonance at δ 2.7, essentially unchanged from that of **3a**, δ 1.3. In contrast, ^{29}Si resonances for W-SiMe₂Cl groups are observed in the range δ 55.8–70.0.⁹ Chlorination occurs at room temperature with reaction times ranging from 1–3 h, again depending upon the sterics of the groups on germanium. The isolated yields range from 68 to 87%. Additionally, **4a** has been structurally characterized by single-crystal X-ray diffraction methods (vide infra).

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for Compound 4a

W-Ge	2.542(1)	Ge-C12	1.987(13)
W-Si	2.591(3)	Si-C13	1.902(14)
W-C1	2.263(9)	Si-C14	1.915(11)
W-C2	2.290(8)	Si-C15	1.853(14)
W-C3	2.302(11)	C1-C2	1.415(15)
W-C4	2.296(11)	C1-C5	1.407(13)
W-C5	2.290(9)	C2-C3	1.359(16)
W-C6	2.309(11)	C3-C4	1.375(17)
W-C7	2.274(11)	C4-C5	1.403(15)
W-C8	2.302(10)	C6-C7	1.376(16)
W-C9	2.291(10)	C6-C10	1.375(16)
W-C10	2.296(9)	C7-C8	1.438(20)
Ge-Cl	2.341(4)	C8-C9	1.403(15)
Ge-C11	1.966(13)	C9-C10	1.385(16)
Ge-W-Si	85.9(1)	C14-Si-C15	102.8(5)
W-Ge-Cl	109.5(1)	C2-C1-C5	106.9(9)
W-Ge-C11	123.0(4)	C1-C2-C3	108.7(9)
W-Ge-C12	122.2(3)	C2-C3-C4	108.8(10)
Cl-Ge-C11	95.3(4)	C3-C4-C5	108.9(10)
Cl-Ge-C12	95.4(4)	C1-C5-C4	106.8(9)
C11-Ge-C12	104.6(5)	C7-C6-C10	108.6(11)
W-Si-C13	112.7(4)	C6-C7-C8	108.3(10)
W-Si-C14	116.8(4)	C7-C8-C9	105.5(10)
W-Si-C15	118.1(4)	C8-C9-C10	108.8(10)
C13-Si-C14	102.3(6)	C6-C10-C9	108.8(9)
C13-Si-C15	101.9(7)		



The ratio does not change with further heating. In addition to **4a** (60%), the mixture contains $\text{Cp}_2\text{W}(\text{SiMe}_2\text{Cl})(\text{GeMe}_3)$ (16%), $\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{GeMe}_3)$ (12%), and $\text{Cp}_2\text{W}(\text{SiMe}_2\text{Cl})(\text{GeMe}_2\text{Cl})$ (12%). The former results from the *intramolecular* exchange of chloride and methyl groups between the germyl and silyl ligands of **4a**. The latter two compounds are produced in equal amounts from the *intermolecular* exchange of chloride and methyl groups. No other products are observed by ^1H NMR.

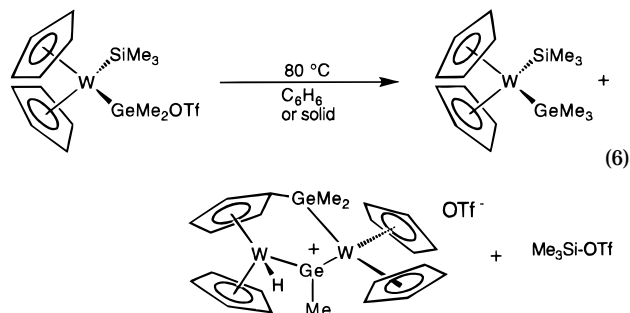
The presence of **2** was confirmed by comparison of the ^1H NMR with an authentic sample synthesized independently. However, there are no obvious routes to prepare $\text{Cp}_2\text{W}(\text{SiMe}_2\text{Cl})(\text{GeMe}_2\text{Cl})$ and $\text{Cp}_2\text{W}(\text{SiMe}_2\text{Cl})(\text{GeMe}_3)$; thus assignment of the structures is based on ^1H NMR. Attempts to identify the corresponding parent ions in the mass spectrum of the equilibrium mixture were thwarted by the ready fragmentation of the silyl and germyl ligands, even when using chemical ionization techniques.

It has been previously reported that Lewis acids such as $\text{B}(\text{C}_6\text{F}_5)_3$ greatly accelerate redistribution in $\text{Cp}_2\text{W}(\text{SiR}_2\text{X})(\text{SiMe}_3)$ complexes.⁸ Indeed, addition of 10% $\text{B}(\text{C}_6\text{F}_5)_3$ to a benzene solution of **4a** generates the equilibrium mixture within seconds at 25 °C.

Thermolysis of complexes with larger substituents on the germyl ligand, **4b,c**, results in the formation of a large number of products presumably arising from both inter- and intramolecular rearrangements and subsequent decomposition reactions at the high temperature required.

The triflate analog of **4a**, $\text{Cp}_2\text{W}(\text{SiMe}_3)(\text{GeMe}_2\text{OTf})$ (**5a**), does not follow the same course upon thermolysis,

but rather undergoes a more complex transformation as indicated in eq 6. The products are Me_3SiOTf , **2**, and



the dimeric species $[\text{Cp}_2\text{W}(\mu\text{-}\eta^5, \eta^1\text{-C}_5\text{H}_4\text{GeMe}_2)(\mu\text{-Ge-Me})\text{W}(\text{Cp})(\text{H})]^+[\text{OTf}]^-$ (**7**). Interestingly, the reaction proceeds equally well at 80 °C in benzene solution or in the solid state, and **7** has been obtained in 63% yield (93% of the theoretical yield based on the stoichiometry of eq 6).

The dimeric compound, **7**, is an orange solid, insoluble in most organic solvents but slightly soluble in acetonitrile at room temperature. The ^1H NMR spectrum was taken in supersaturated solutions of CD_3CN and exhibits three singlets for the Cp rings and three broad multiplets for the substituted C_5H_4 ring. The resonance for the remaining C_5H_4 proton is obscured by the Cp signals. There are two singlets corresponding to the two inequivalent methyl groups on the germanium attached to the Cp ring and a single resonance for the methyl group on the germanium which bridges the two tungsten metal centers. A singlet corresponding to the tungsten hydride is observed at $\delta -10.8$. The structure of **7** has been unambiguously determined by single-crystal X-ray diffraction methods, reported elsewhere.¹³

Discussion

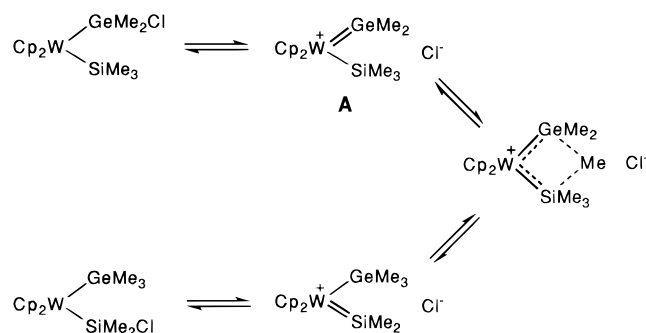
The reaction of the tungstenocene silene complex $\text{Cp}_2\text{W}(\eta^2\text{-SiMe}_2=\text{CH}_2)$ with hydridogermanes is a high-yield, convenient route to silyl germyl complexes. Compounds containing Ge-H bonds can be readily functionalized to the chloride and triflate derivatives via well-precedented reactions. The formation of the germyl silyl complexes involves the net addition of a Ge-H bond across the W-C bond of $\text{Cp}_2\text{W}(\eta^2\text{-SiMe}_2=\text{CH}_2)$. The analogous addition of hydrosilanes has been shown to be an effective route to the bis(silyl) complexes. Previous studies of the reaction of hydrogen and silanes with the coordinatively saturated $\text{Cp}_2\text{W}(\eta^2\text{-SiMe}_2=\text{CH}_2)$ indicate that the reaction initially proceeds by a reversible silicon to Cp migration which creates a vacant coordination site.¹⁴ It is likely that the reactions of germanes with $\text{Cp}_2\text{W}(\eta^2\text{-SiMe}_2=\text{CH}_2)$ follow a similar course.

The formation of $\text{Cp}_2\text{W}(\text{SiMe}_2\text{Cl})(\text{GeMe}_3)$ from **4a** results from the intramolecular exchange of methyl and chloride substituents and is analogous to the reactivity observed in the closely related bis(silyl) systems. Investigation of the intramolecular migrations in the tungstenocene bis(silyl) systems indicates that the rear-

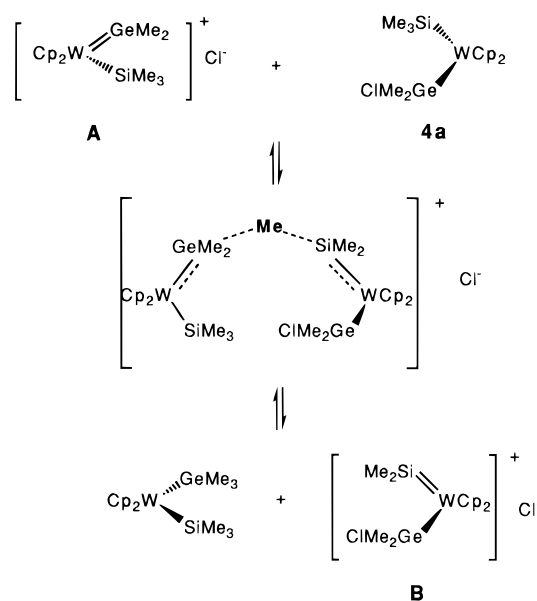
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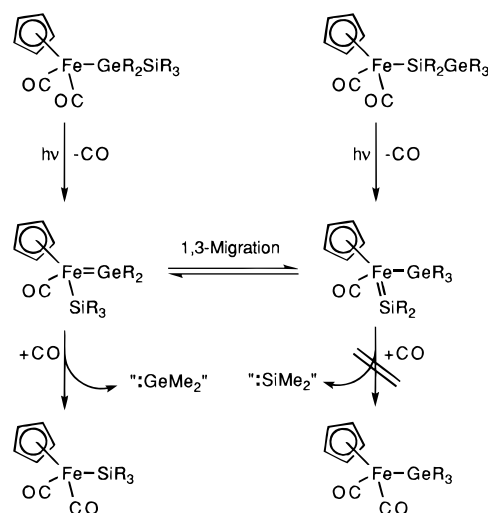
Scheme 1



Scheme 2



Scheme 3



rangements proceed via a cationic silylene silyl complex formed by X^- dissociation from a $M-Si-X$ group ($X^- = Cl^-, OTf^-$). Once formed, this electrophilic intermediate can undergo facile 1,3-methyl migrations between the two silicon centers. This type of 1,3 - migration has great precedent in other electron-deficient silicon systems¹⁵ and was first proposed in a metal silyl silylene complex by Pannell and co-workers in 1986.^{5a} An analogous mechanism is most likely operative in the present silyl germyl case.

The equilibrium established in the thermolysis of **4a** (eq 5) appears complex at first glance but can be readily understood in terms of two processes. Initially, chloride dissociation forms a germylene silyl intermediate, **A** (Scheme 1). Migration of the methyl group could then occur via a symmetrical intermediate or transition state in which the methyl group bridges the germanium and silicon centers. Stable analogs containing methoxy groups bridging iron(germylene)(silylene) complexes have been reported by Ogino, Tobita, and co-workers.¹⁶ Cleavage of the methyl-bridged species would generate a germyl silylene cation, and association of the chloride would then yield the observed rearranged product, $Cp_2W(SiMe_2Cl)(GeMe_3)$.

The presence of **2** and $Cp_2W(SiMe_2Cl)(GeMe_2Cl)$ in the equilibrium mixture following thermolysis of **4a** requires the exchange of methyl and chloride groups between two different tungsten complexes. This can be accommodated by a modified mechanism (Scheme 2) in which the electrophilic germylene intermediate, **A**, abstracts a methyl group from another equivalent of **4a** to yield **2** and a germyl silylene, **B**. Coordination of the chloride to **B** would then form $Cp_2W(SiMe_2Cl)(GeMe_2Cl)$. Tilley and co-workers have recently directly observed intermolecular methyl migration between $Cp^*(PMe_3)_2RuSiMe_3$ and the stable silylene complex $[Cp^*(PMe_3)_2RuSiPh_2]^+$.¹⁷

Recent studies by Pannell and co-workers describe the photolysis of $FpGeR_2SiR_3$ and $FpSiR_2GeR_3$ ($Fp \equiv (\eta^5-C_5H_5)Fe(CO)_2$) systems and provide evidence for the formation of silyl germylene and germyl silylene intermediates which undergo 1,3-migrations of the substitu-

ents between the silicon and germanium ligands (Scheme 3).^{7a} These photolytic rearrangements are complicated somewhat by the apparent loss of $SiMe_2$ and $GeMe_2$ units during the reaction; however, the almost exclusive formation of the metal silyl product has been interpreted to mean that GeR_2 expulsion is the favored process in the system and is attributed to the thermodynamic stability of the germylene intermediate over that of the silylene intermediate.

In the case of the intramolecular exchange between **4a** and $Cp_2W(SiMe_2Cl)(GeMe_3)$, the equilibrium is directly observed and is determined by the relative stabilities of these ground state complexes, not the stabilities of intermediate silylene and germylene complexes. The slight preference for **4a** most likely reflects a steric advantage: the shortening of the bond to tungsten caused by the chloride substituent on either silicon or germanium results in increased steric hindrance between the silyl or germyl and the Cp ligands. Shortening of the tungsten germyl bond is more easily accommodated than the silyl because $W-Ge$ bonds are inherently longer than analogous $W-Si$ bonds.

Although most of the features of these tungsten germyl silyl complexes parallel those of the bis(silyl)

(15) (a) Eaborn, C.; Happer, D. A. R.; Hopper, S. P.; Safa, K. D. *J. Organomet. Chem.* **1980**, *188*, 179. (b) Eaborn, C.; Hopper, S. P. *J. Organomet. Chem.* **1980**, *192*, 27. (c) Eaborn, C.; Lickiss, P. D.; Ramadan, N. A. *J. Chem. Soc., Perkin. Trans. 2* **1984**, 267. (d) Avent, A. G.; Bott, S. G.; Ladd, J. A.; Lickiss, P. D.; Pidcock, A. *J. Organomet. Chem.* **1992**, *427*, 9. (e) Wiberg, N. *J. Organomet. Chem.* **1984**, *273*, 141. (f) Wiberg, N.; Wagner, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229. (g) Wiberg, N.; Wagner, G.; Riede, J.; Müller, G. *Organometallics* **1987**, *6*, 32.

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(17) Grumbine, S. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 6951.

analogs, there is one noteworthy difference. Alkyl group redistributions in the bis(silyl) system were exclusively intramolecular, but both inter- and intramolecular migrations are observed in the tungsten germyl silyl complexes. The difference in the reactivity of the two systems is probably dependent on the stability of the intermediates. It is reasonable to suppose that a cationic germylene silyl complex (e.g. **A**) is more stable and longer lived than a silylene silyl generated by dissociation of X^- from $Cp_2W(SiMe_3)(SiR_2X)$ and that the germylene has a greater opportunity to undergo bimolecular reactions such as intermolecular methyl transfer.

Experimental Section

General Considerations. All manipulations were carried out under dry nitrogen using high-vacuum line or Schlenk techniques or a glovebox under an atmosphere of prepurified N_2 . Glassware was oven-dried before use. Petroleum ether (boiling range 35–65 °C), pentane, benzene, and toluene were freshly distilled from sodium/benzophenone ketyl. $Cp_2W(\eta^2-SiMe_2=CH_2)$ was prepared according to the literature method.^{14a} Germanes (Gelest, Inc.) were dried over 4-Å molecular sieves and degassed before use. Organogermanes were prepared by the reduction of the appropriate chlorogermane with lithium aluminum hydride. Routine 1H NMR spectra were obtained using IBM Bruker AC 250 or AM 200 spectrometers. ^{13}C NMR spectra were obtained on an IBM Bruker AM 500 spectrometer. ^{29}Si spectra were obtained at 40 MHz on a Bruker AF-200 spectrometer with a broad-band multinuclear probe using the DEPT pulse sequence. Benzene- d_6 was used as an NMR solvent unless otherwise indicated. The 1H , ^{13}C , ^{29}Si spectra were referenced to $SiMe_4$. Elemental analyses were performed by Robertson Laboratories.

Preparation of $Cp_2W(SiMe_3)(GeMe_3)$ (2**).** To a toluene solution containing $Cp_2W(\eta^2-SiMe_2=CH_2)$ (350 mg, 0.90 mmol) was added $GeMe_3H$ (0.35 mL, 2.95 mmol). After stirring overnight at room temperature the volatiles were removed and the solids recrystallized from toluene/petroleum ether to yield 312 mg (68%) of orange-yellow solid. Anal. Calcd for $C_{16}H_{28}WSiGe$: C, 38.06; H, 5.59. Found: C, 38.00; H, 5.60.

Preparation of $Cp_2W(SiMe_3)(GeMe_2H)$ (3a**).** To a toluene solution containing $Cp_2W(\eta^2-SiMe_2=CH_2)$ (900 mg, 2.33 mmol) was added $GeMe_2H_2$ (4.60 mmol). After the solution was stirred for 18 h at 25 °C, the volatiles were removed and the solids recrystallized from toluene/petroleum ether to yield 810 mg (71%) of yellow crystals. Anal. Calcd for $C_{15}H_{26}WSiGe$: C, 36.70; H, 5.34. Found: C, 37.08; H, 5.37.

Preparation of $Cp_2W(SiMe_3)(Ge^tBu_2H)$ (3b**).** To a toluene solution containing $Cp_2W(\eta^2-SiMe_2=CH_2)$ (1.00 g, 2.59 mmol) was added $Ge^tBu_2H_2$ (5.2 mmol). After the solution was stirred for 5 days at room temperature, the volatiles were removed and the solids recrystallized from pentane to yield 960 mg (65%) of bright yellow crystals. Anal. Calcd for $C_{21}H_{38}WSiGe$: C, 43.86; H, 6.66. Found: C, 43.82; H, 6.64.

Preparation of $Cp_2W(SiMe_3)(GePh_2H)$ (3c**).** To a toluene solution containing $Cp_2W(\eta^2-SiMe_2=CH_2)$ (750 mg, 1.94 mmol) was added $GePh_2H_2$ (4.0 mmol). After the solution was stirred for 12 h at 25 °C, the volatiles were removed and the solids were recrystallized from toluene/petroleum ether to yield 950 mg (80%) of yellow solid.

Preparation of $Cp_2W(SiMe_3)(GeMe_2Cl)$ (4a**).** To a toluene solution containing $Cp_2W(SiMe_3)(GeMe_2H)$ (570 mg, 1.16 mmol) was added CCl_4 (1.59 g, 10.36 mmol). After the solution was stirred for 10 min at room temperature, the volatiles were removed and the solids recrystallized from toluene/petroleum ether to yield 510 mg (83%) of yellow crystals. Anal. Calcd for $C_{15}H_{25}WClSiGe$: C, 34.29; H, 4.80. Found: C, 34.54; H, 4.71.

Preparation of $Cp_2W(SiMe_3)(Ge^tBu_2Cl)$ (4b**).** To a toluene solution containing $Cp_2W(SiMe_3)(Ge^tBu_2H)$ (0.45 g, 0.78 mmol) was added CCl_4 (0.25 g, 1.63 mmol). After the solution was stirred for 2 h at room temperature, the volatiles were removed and the solids recrystallized from petroleum ether to yield 430 mg (681) of yellow crystals. Anal. Calcd for $C_{21}H_{37}WSiGeCl$: C, 41.38; H, 6.12. Found: C, 41.03; H, 5.87.

Preparation of $Cp_2W(SiMe_3)(GePh_2Cl)$ (4c**).** To a toluene solution containing $Cp_2W(SiMe_3)(GePh_2H)$ (750 mg, 1.22 mmol) was added CCl_4 (0.31 g, 2.04 mmol). After the solution was stirred for 4 h at room temperature the volatiles were removed and the solids were recrystallized from toluene/petroleum ether to yield 610 mg (77%) of yellow solid. Anal. Calcd for $C_{25}H_{29}WSiGeCl$: C, 46.23; H, 4.50. Found: C, 46.39; H, 4.45.

Preparation of $Cp_2W(SiMe_3)(GeMe_2OTf)$ (5a**).** To a benzene solution containing $Cp_2W(SiMe_3)(GeMe_2Cl)$ (260 mg, 0.49 mmol) was added trimethylsilyl trifluoromethanesulfonate (230 mg, 1.03 mmol). After the solution was stirred for 1 h at room temperature the volatiles were removed and the solids recrystallized from toluene to yield 276 mg (87%) of pale yellow solid. Anal. Calcd for $C_{16}H_{25}O_3SF_3SiGeW$: C, 30.08; H, 3.94. Found: C, 30.21; H, 3.86.

Preparation of $Cp_2W(SiMe_2OTf)(Ge^tBu_2Me)$ (6b**).** To a toluene solution containing $Cp_2W(SiMe_3)(Ge^tBu_2Cl)$ (0.287 g, 0.40 mmol) was added trimethylsilyl trifluoromethanesulfonate (340 mg, 1.56 mmol). After the solution was stirred for 12 h at 70 °C the volatiles were removed and the solids were recrystallized twice from toluene/petroleum ether to yield 230 mg (67%) of pale yellow solid. Anal. Calcd for $C_{22}H_{37}WSiGeO_3SF_3$: C, 36.54; H, 5.16. Found: C, 36.19; H, 4.77.

Preparation of $[Cp_2W(\eta^5, \eta^1-C_5H_4GeMe_2)(\mu-GeMe)W(Cp)(H)]^+ [OTf]^-$ (7**).** $Cp_2W(SiMe_3)(GeMe_2OTf)$ (85 mg, 0.13 mmol) was heated at 80 °C for 15 h in an evacuated glass bomb (with no solvent.) The volatiles (TMS–OTf) were removed, and the orange solid was washed with toluene and petroleum ether to remove $Cp_2W(SiMe_3)(GeMe_3)$, yielding 33 mg (79%) of an orange solid. Anal. Calcd for $C_{24}H_{29}W_2Ge_2O_3F_3S$: C, 29.80; H, 3.02. Found: C, 29.92; H, 2.71.

Structure Determination of **4a.** A single crystal of suitable size was grown from toluene/petroleum ether at –35 °C and sealed in 0.5-mm thin-walled Pyrex capillary in the glovebox, and the capillary was mounted on the diffractometer. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 25 accurately centered reflections with $2\theta > 25^\circ$. Crystal data are summarized in Table 2.

Diffraction data were collected at 295 K on an Enraf-Nonius CAD-4 diffractometer employing $Mo K_\alpha$ radiation filtered through a highly oriented graphite crystal monochromator. A linear correction for decay was applied on the basis of the intensities of three standard reflections measured at intervals of 3500 s of X-ray exposure. The raw intensities were corrected for Lorentz and polarization effects by using the Enraf-Nonius MolEN¹⁸ package. Empirical absorption corrections based on ψ -scans were also applied.

All calculations were performed on a DEC MicroVax 3100 computer using the Enraf-Nonius MolEN package. The full-matrix least squares refinement was based on F , and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights (w) were taken as $1/\sigma^2(F_o)$. Atomic scattering factors and complex anomalous dispersion corrections were taken from refs 19–21. Agreement factors are defined as $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$ and $R_2 = [\sum w|F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$. The goodness-of-fit is

(18) MolEn, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, The Netherlands, 1990.

(19) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(20) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

defined as $GOF = [\sum w(|F_o| - |F_c|)^2 / (N_o - N_p)]^{1/2}$, where N_o and N_p are the number of observations and parameters.

Of the total of 4552 reflections, 3183 unique reflections with $F^2 > 3\sigma(F^2)$ were used during subsequent structure refinement. The structure was solved by standard heavy-atom Patterson techniques followed by weighted Fourier syntheses. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included as constant contributions to the structure

(21) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

factors and were not refined. Refinement converged to $R_1 = 0.031$ and $R_2 = 0.055$.

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Supporting Information Available: Tables of positional and B parameters, anisotropic thermal parameters, and intramolecular distances and angles for **4a** (6 pages). Ordering information is given on any current masthead page.

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