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(Silylgermyl)methyl and (Germylsilyl)methyl Chemistry. Synthesis and Rearrangements of $LMCH_2GeMe_2SiMe_3$ and $LMCH_2SiMe_2GeMe_3$ [$LM = (\eta^5\text{-}C_5H_5)M(CO)_n$; M = Fe ($n$ = 2), W (n = 3)]

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Isomeric compounds of the type $LMCH_2GeMe_2SiMe_3$ and $LMCH_2SiMe_2GeMe_3$ [$LM = (\eta^5\text{-}C_5H_5)M(CO)_n$; M = Fe (Fp) ($n$ = 2); W (Wp) (n = 3)] have been synthesized and characterized. The Fp complexes $FpCH_2GeMe_2SiMe_3$ and $FpCH_2SiMe_2GeMe_3$ underwent a photochemical rearrangement to $FpGeMe_2CH_2SiMe_3$ and $FpSiMe_2CH_2GeMe_3$, respectively. The tungsten complex $WpCH_2GeMe_2SiMe_3$ also underwent a photochemical rearrangement to form $WpGeMe_2CH_2SiMe_3$, while the isomeric $WpCH_2SiMe_2GeMe_3$ photochemically eliminated $Me_2Si{=}CH_2$ to form $WpGeMe_3$. The same β-elimination occurred thermally, and the silene $Me_2Si{=}CH_2$ was trapped by *tert*-butyl alcohol to produce $Me_3SiOCMe_3$. Trace amounts of $Me_3SiGeMe_3$ were obtained via heterolytic cleavage of the metal–carbon bond. The results are discussed in terms of Si–M, Si–C, Ge–M, and Ge–C bond strengths, as well as silene–metal and germene–metal bond strengths.

Introduction

Given the interest in silicon–germanium materials, studies of compounds containing Si–Ge bonds are relatively rare despite the fact that the initial report of such a compound was in 1934.[1] Mass spectral studies on Si–Ge compounds by Glockling and co-workers in 1968 reported ligand exchange between the two group 14 elements,[2a] a result confirmed by other workers.[2b,c] Later the Kumada group investigated the synthesis and alcoholysis of ferrocene derivatives of Si–Ge compounds;[3] however, it was not until 1986 that the Si–Ge bond was first characterized structurally.[4] Since that time we, and the Ogino group, have investigated the photochemical properties of transition metal complexes containing the Si–Ge grouping directly bonded to a metal center, i.e. $FpGeMe_2SiMe_3$ and $FpSiMe_2GeMe_3$ [$Fp = (\eta^5\text{-}C_5H_5)Fe(CO)_2$]. Via silylgermylene and germyl–silylene intermediates photolysis led to the elimination of either $GeMe_2$ or $SiMe_2$, with a preponderance of $GeMe_2$.[5a,b] An extension of this study to $FpSiMe_2GeMe_2Fp$ also illustrated that germylene formation is preferred and the initial product of photochemical treatment led to $(\eta^5\text{-}C_5H_5)Fe(CO)(\mu\text{-}CO)(\mu\text{-}GeMe(SiMe_3))Fe(CO)(\eta^5\text{-}C_5H_5)$ prior to formation of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}GeMe_2)(\mu\text{-}SiMe_2)$.[5c] Recent studies, including those by Baines and co-workers aimed at the synthesis and study of compounds containing a silicon–germanium double bond, further attest to a growing interest in compounds with such heteronuclear inter-group 14 compounds.[6] As part of our interest in such compounds, we report the synthesis of the first isomeric carbon functional compounds $XCH_2GeMe_2SiMe_3$ and $XCH_2SiMe_2GeMe_3$ (X = Cl, I), the use of these halomethyl compounds to form transition metal derivatives $LM[CH_2Si(Ge)Me_2Ge(Si)Me_3]$ [LM = Fp, $(\eta^5\text{-}C_5H_5)W(CO)_3$ (Wp)], and the thermal and photochemical rearrangements of these metal complexes.

Results and Discussion

The syntheses of the chloromethyl compounds were accomplished with good to moderate yields via the recently developed use of *in situ* generated (chloromethyl)lithium and the corresponding halosilane or halogermane (eqs 1 and 2).[7] Trace amounts of the corresponding butyl derivatives were obtained.

$$ClGeMe_2SiMe_3 + [ClCH_2]^-Li^+ \rightarrow ClCH_2GeMe_2SiMe_3 + LiCl \quad (1)$$

$$ClSiMe_2GeMe_3 + [ClCH_2]^-Li^+ \rightarrow ClCH_2SiMe_2GeMe_3 + LiCl \quad (2)$$

The chloromethyl compounds were used as reagents for further derivatization by the $[Fp]^-Na^+$ salt (eqs 3 and 4).

The syntheses of the analogous tungsten complexes required the use of the ((iodomethyl)germyl)silane and ((iodomethyl)silyl)germane compounds (prepared by treatment of the corresponding chloromethyl compounds with NaI in acetone; eqs 5 and 6).

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$$[Fp]^{-}Na^{+} + ClCH_2GeMe_2SiMe_3 \rightarrow FpCH_2GeMe_2SiMe_3\ (\mathbf{I}) + NaCl \quad (3)$$

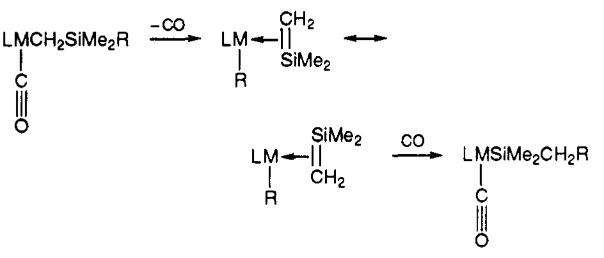
$$[Fp]^{-}Na^{+} + ClCH_2SiMe_2GeMe_3 \rightarrow FpCH_2SiMe_2GeMe_3\ (\mathbf{II}) + NaCl \quad (4)$$

$$[Wp]^{-}Na^{+} + ICH_2GeMe_2SiMe_3 \rightarrow WpCH_2GeMe_2SiMe_3\ (\mathbf{III}) + NaI \quad (5)$$

$$[Wp]^{-}Na^{+} + ICH_2SiMe_2GeMe_3 \rightarrow WpCH_2SiMe_2GeMe_3\ (\mathbf{IV}) + NaI \quad (6)$$

The new complexes have spectroscopic and analytical data in agreement with their proposed structures (Table I). The synthesis of **III** was accompanied by formation of 10–20% of (η^5-C_5H_5)W(CO)$_3$Me which could be removed by sublimation. This result is similar to that reported by Lappert et al. during an attempted synthesis of (η^5-C_5H_5)Mo(CO)$_3$CH$_2$SiMe$_3$ where, rather than the anticipated product, only (η^5-C_5H_5)Mo(CO)$_3$Me was obtained.[8]

The isomeric metal-substituted inter-group 14 compounds present a unique opportunity to assess the chemical similarities and distinctions between the two non-carbon group 14 elements. In studying the chemistry of the new systems, it is instructive to note the properties of the related Si–Si-bonded analogs (the Ge–Ge analogs are presently being investigated in our laboratory). The key early report by Kumada et al. demonstrated the capacity of a (halomethyl)disilane, $ClCH_2SiMe_2SiMe_3$, to undergo a facile $AlCl_3$-catalyzed isomerization to $ClSiMe_2CH_2SiMe_3$.[9] This rearrangement was driven by the greater Si–Cl vs C–Cl and Si–C vs Si–Si bond energies, approximately 40 and 90 kJ/mol, respectively. Much later we showed that related transition metal complexes, e.g. $FpCH_2(SiMe_2)_nSiMe_3$, could undergo a similar rearrangement upon photochemical irradiation to form $FpSiMe_2CH_2(SiMe_2)_{n-1}SiMe_3$.[10] The reaction proceeds by initial photodissociation of CO to form a reactive 16e$^-$ intermediate that via β-elimination forms transient silyl–silene complexes. Recoordination of CO, coupled with rotation of the silene moiety, resulted in the product (eq 7).



(7)

R = SiMe$_3$, SiMe$_2$SiMe$_3$

Such transition metal chemistry is related to the rearrangements of analogous (hydridosilyl)methyl complexes (R = H in eq 7), in which intermediate silene complexes have been observed spectroscopically, isolated, and in some related cases characterized via single-crystal X-ray crystallography.[11,12]

The new compounds **I**–**IV** exhibit chemistry both similar to and different from that of the disilylmethyl complexes noted above. The ((silylgermyl)methyl)metal complexes, $LMCH_2GeMe_2SiMe_3$ (**I**, **III**), undergo photochemical isomerizations to $LMGeMe_2CH_2SiMe_3$ (eq 8).

$$LMCH_2GeMe_2SiMe_3 \xrightarrow{h\nu} LMGeMe_2CH_2SiMe_3 \quad (8)$$

$$LM = Fp\ (\mathbf{I} \rightarrow \mathbf{V}),\ Wp\ (\mathbf{III} \rightarrow \mathbf{VI})$$

The ((germylsilyl)methyl)metal complexes $LMCH_2SiMe_2GeMe_3$ (**II**, **IV**), exhibit different chemistry. While photochemical irradiation of **II** resulted in a rearrangement (eq 9), **IV** underwent a high-yield photochemical loss of the elements of dimethylsilene with concurrent formation of $WpGeMe_3$ (a previously reported complex;[13] eq 10).

$$FpCH_2SiMe_2GeMe_3\ (\mathbf{II}) \xrightarrow{h\nu} FpSiMe_2CH_2GeMe_3\ (\mathbf{VII}) \quad (9)$$

$$WpCH_2SiMe_2GeMe_3\ (\mathbf{IV}) \xrightarrow{h\nu} WpGeMe_3 + [Me_2SiCH_2] \quad (10)$$

Gas chromatographic/mass spectral analysis of $WpCH_2SiMe_2GeMe_3$ proved interesting since a fresh sample produced a GC/MS analysis equivalent to $WpGeMe_3$, from both the GC and the MS portions. The infrared and NMR data for **IV** were in total accord with the formulation $WpCH_2SiMe_2GeMe_3$; thus it appeared that, in addition to the photochemical expulsion of [Me_2SiCH_2], a similar reaction occurred upon injection of **IV** into the GC instrument. In a separate experiment we heated **IV** (refluxing decane solution), and NMR and IR analysis indicated that the product of this thermal reaction was indeed $WpGeMe_3$ (eq 11). Clearly **IV** exhibits both a thermal and photochemical β-elimination. The facility of this reaction has precluded our obtaining a satisfactory elemental analysis for **IV**; the results always coincide with the elemental analysis for $WpGeMe_3$.

$$WpCH_2SiMe_2GeMe_3\ (\mathbf{IV}) \xrightarrow{\Delta} WpGeMe_3 + [Me_2SiCH_2] \quad (11)$$

By conducting the thermal reaction of **IV** in *tert*-butyl alcohol, we have trapped the silene portion of the reaction as $Me_3SiOCMe_3$ (eq 12), identified by comparison of its spectral data with those of an authentic sample.

$$WpCH_2SiMe_2GeMe_3\ (\mathbf{IV}) \xrightarrow{t\text{-BuOH}} WpGeMe_3 + Me_3SiOCMe_3 \quad (12)$$

Small amounts of WpMe, $Me_3GeSiMe_3$, and $Me_3GeOCMe_3$ were observed in the GC/mass spectral analysis

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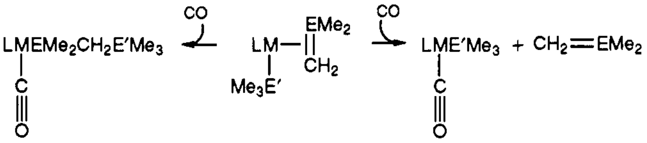
Table I. Spectroscopic and Analytical Data for New Complexes[a]

	$ClCH_2GeMe_2SiMe_3$: 72% Yield; Bp 78 °C/25 mmHg. Anal. Found (Calcd): C, 33.05 (32.00); H, 7.52 (7.55)
^1H NMR	δ 0.09 ($SiMe_3$), 0.22 ($GeMe_2$), 2.64 (CH_2)
^{13}C NMR	δ −5.34 ($GeMe_2$), −1.52 ($SiMe_3$), 30.6 (CH_2)
^{29}Si NMR	δ −10.7
mass	*m/e* 211 (M − Me, 10%), 177 (191, M − Cl, 1%), 89 (GeMe, 20%), 73 ($SiMe_3$, 100%)
	$ClCH_2SiMe_2GeMe_3$: 70% Yield; Bp 78 °C/25 mmHg. Anal. Found (Calcd): C, 32.85 (32.00) H, 7.51 (7.55)
^1H NMR	δ 0.09 ($SiMe_2$), 0.19 ($GeMe_3$), 2.64 (CH_2)
^{13}C NMR	δ −4.79 ($SiMe_2$), −2.96 ($GeMe_3$), 30.8 (CH_2)
^{29}Si NMR	δ −7.63
mass	*m/e* 211 (M − Me, 60%), 191 (M − Cl, <1%), 119 (Me_3Ge, 90%), 73 (Me_3Si, 100%)
	$ICH_2GeMe_2SiMe_3$: 57% Yield; Bp 96–7 °C/25 mmHg. Anal. Found (Calcd): C, 23.38 (22.76); H, 5.60 (5.37)
^1H NMR	δ 0.33 ($SiMe_3$), 0.45 ($GeMe_2$), 2.19 (CH_2)
^{13}C NMR	δ −15.1 (CH_2), −1.31 ($SiMe_3$), −0.64 ($GeMe_2$)
^{29}Si NMR	δ −10.5
mass	*m/e* 303 (M − Me, 45%), 191 (M − I, 45%), 119 ($GeMe_3$, 30%), 73 (Me_3Si, 100%)
	$ICH_2SiMe_2GeMe_3$: 60% Yield; Bp 98–100 °C/25 mmHg. Anal. Found (Calcd): C, 22.26 (22.76); H, 5.17 (5.37)
^1H NMR	δ 0.34 ($SiMe_2$), 0.43 ($GeMe_3$), 2.06 (CH_2)
^{13}C NMR	δ −12.5 (CH_2), −2.73 ($GeMe_3$), −2.24 ($SiMe_2$)
^{29}Si NMR	δ −6.1
mass	*m/e* 303 (M − Me, 60%), 191 (M − I, 60%), 119 ($GeMe_3$, 65%), 73 ($SiMe_3$, 100%)
	$FpCH_2GeMe_2SiMe_3$ (I): 28% Yield. Anal. Found (Calcd): C, 41.97 (42.58); H, 5.98 (6.00)
^1H NMR	δ 0.21 ($SiMe_3$), 0.34 ($GeMe_2$), 0.55 (CH_2), 4.14 (η^5-C_5H_5)
^{13}C NMR	δ −21.6 (CH_2), −1.28 ($SiMe_3$), 6.45 ($GeMe_2$), 84.9 (η^5-C_5H_5), 217.6 (CO)
^{29}Si NMR	δ −11.7
IR	ν(CO) 2010, 1959
	$FpCH_2SiMe_2GeMe_3$ (II): 37% Yield. Anal. Found (Calcd): C, 42.06 (42.58); H, 6.01 (6.00)
^1H NMR	δ −0.19 (CH_2), 0.23 ($SiMe_2$ + $GeMe_3$), 4.16 (η^5-C_5H_5)
^{13}C NMR	δ −24.9 (CH_2), −2.51 ($GeMe_3$), 0.25 ($SiMe_2$), 84.8 (η^5-C_5H_5), 217.5 (CO)
^{29}Si NMR	δ 0.64
IR	ν(CO) 2012, 1961
	(η^5-C_5H_5)$W(CO)_3CH_2GeMe_2SiMe_3$ (III): 40% Yield; Mp 53 °C. Anal. Found (Calcd): C, 32.15 (32.17); H, 4.42 (4.21)
^1H NMR	δ 0.27 (CH_2), 0.34 ($SiMe_3$), 0.51 ($GeMe_2$), 4.68 (η^5-C_5H_5)
^{13}C NMR	δ −36.4 (CH_2), −1.30 ($SiMe_3$), 0.04 ($GeMe_2$), 91.5 (η^5-C_5H_5), 218.2, 230.2 (CO)
^{29}Si NMR	δ −10.9
IR	ν(CO) 2018, 1928
	(η^5-C_5H_5)$W(CO)_3CH_2SiMe_2GeMe_3$ (IV): 44% Yield; Mp 55 °C
^1H NMR	δ 0.33 (CH_2), 0.63 ($GeMe_3$), 0.64 ($SiMe_2$), 4.72 (η^5-C_5H_5)
^{13}C NMR	δ −38.9 (CH_2), −2.65 ($GeMe_3$), 1.34 ($SiMe_2$), 91.46 (η^5-C_5H_5), 218.6, 229.9 (CO)
^{29}Si NMR	δ 0.94
IR	ν(CO) 2018, 1928
	$FpGeMe_2CH_2SiMe_3$ (V): 80% Yield
^1H NMR	δ 0.17 ($SiMe_3$), 0.28 (CH_2), 0.67 ($GeMe_2$), 4.06 (η^5-C_5H_5)
^{13}C NMR	δ 0.56 ($SiMe_3$), 7.62 ($GeMe_2$), 11.9 (CH_2), 83.0 (η^5-C_5H_5), 216.5 (CO)
^{29}Si NMR	δ 1.10
IR	ν(CO) 1996, 1946
	(η^5-C_5H_5)$W(CO)_3GeMe_2CH_2SiMe_3$ (VI): 60% Yield; Mp 45–7 °C. Anal. Found (Calcd): C, 32.08 (32.16); H, 3.97 (4.21)
^1H NMR	δ 0.36 ($SiMe_3$), 0.46 (CH_2), 0.85 ($GeMe_2$), 4.55 (η^5-C_5H_5)
^{13}C NMR	δ 1.39 ($SiMe_3$), 6.46 ($GeMe_2$), 10.3 (CH_2), 89.2 (η^5-C_5H_5), 216.6, 220.4 (CO)
^{29}Si NMR	δ 2.2
IR	ν(CO) 1998, 1902
mass	*m/e* 524 (M, 4%), 509 (M − Me, 3%), 191 ($GeMe_2CH_2SiMe_3$, 100%), 119 (Me_3Ge, 11%), 73 (Me_3Si, 22%)
	$FpSiMe_2CH_2GeMe_3$ (VII): 90% Yield. Anal. Found (Calcd): C, 42.54 (42.58); H, 6.24 (6.00)
^1H NMR	δ −0.16 (CH_2), 0.26 ($GeMe_3$), 0.52 ($SiMe_2$), 4.07 (η^5-C_5H_5)
^{13}C NMR	δ 1.27 ($GeMe_3$), 8.25 ($SiMe_2$), 12.1 (CH_2), 83.6 (η^5-(C_5H_5), 216.3 (CO)
^{29}Si NMR	δ 43.9
IR	ν(CO) 1996, 1943

[a] NMR spectra recorded in C_6D_6; IR spectra recorded in hexane.

of the crude reaction products. The mechanism of formation of these compounds was not clear; thus we performed separate experiments involving thermal/photochemical treatment of $FpCH_2SiMe_2SiMe_3$ and $WpGeMe_3$ in the presence of *tert*-butyl alcohol. These experiments resulted in the formation of various compounds as noted via GC/mass spectroscopic analysis. While photochemical treatment of $FpCH_2SiMe_2SiMe_3$ in the presence of *t*-BuOH led only to rearrangement [$FpSiMe_2CH_2SiMe_3$ (95%) and a trace of $Me_3SiOCMe_3$ (<1%); i.e., we did not alter the outcome of the reaction by presenting the postulated intermediate (η^5-C_5H_5)Fe(CO)(CH_2=$SiMe_2$)($SiMe_3$) with *t*-BuOH], thermal treatment resulted in no rearrangement but 9% formation of $Me_3SiOCMe_3$. Thermal treatment of $WpGeMe_3$ with *t*-BuOH led to WpMe (10%). It seems that the Si–Si and Si–Ge bonds in this type of complex are susceptible to cleavage reactions in the presence of *t*-BuOH, accounting for the formation of $Me_3GeOCMe_3$ during the thermal reaction of IV in the presence of *t*-BuOH. Also, the formation of WpMe in the same reaction can be accounted for either by direct cleavage of the $WpCH_2$–($SiMe_2GeMe_3$) bond or, as noted above, via a secondary reaction of $WpGeMe_3$. A detailed study of the thermal reactions of metal silyl, germyl, silylgermyl, and related complexes in the presence of various substrates is being initiated.

The different chemistry exhibited by **IV** compared to complexes **I**–**III** is of interest. We assume that the photochemical rearrangements observed for **I**–**III** proceed via the type of mechanism noted above for the (oligosilyl)methyl complexes (eq 7). In the case of **II**, the intermediacy of $(\eta^5\text{-}C_5H_5)Fe(CO)(Me_2Si{=}CH_2)GeMe_3$ would therefore be involved prior to recombination of CO. For the analogous tungsten complex **IV**, the intermediate would be $(\eta^5\text{-}C_5H_5)W(CO)_2(Me_2Si{=}CH_2)GeMe_3$. It appears that reentry of CO into the germyl–tungsten–silene intermediate causes displacement of the silene and not recombination of the germyl ligand with the silene. The chemistry observed is thus a response to the relative strengths of the group 14–metal bond, the silene(germene)–metal bond, and the Si–C and Ge–C bonds.



The elimination of $CH_2{=}CH_2$ from $LMCH_2CH_2X$ (X = H, R_3Si) is established,[14] whereas no β-eliminations of silenes have been reported. In the case of the Fp complexes **I** and **II**, both the $Me_2Si{=}CH_2$ and $Me_2Ge{=}CH_2$ ligand–Fe bonds are sufficiently stable, and the Fe–$SiMe_3$ or Fe–$GeMe_3$ bonds sufficiently labile, to resist silene(germene) elimination upon recoordination of the CO, and formation of the Si–C or Ge–C bond occurs. For the Wp complexes, the combination of $Me_2Ge{=}CH_2$ ligand–metal bond stability and W–Si lability needed to observe rearrangement for **III** is present; however, the combination of ($Me_2Si{=}CH_2$)–metal bond stability and W–Ge lability is not found for **IV**. We cannot define the specific features of the intermediate $(\eta^5\text{-}C_5H_5)W(CO)_2(Me_2Si{=}CH_2)GeMe_3$ that preclude recombination to form the rearranged complex $(\eta^5\text{-}C_5H_5)W(CO)_3SiMe_2CH_2GeMe_3$, but given the examples of tungsten–silene complexes,[12b] and the rearrangement of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2SiMe_2SiMe_3$ to $(\eta^5\text{-}C_5H_5)W(CO)_2(PPh_3)SiMe_2CH_2SiMe_3$ in the presence of PPh_3, presumably via $(\eta^5\text{-}C_5H_5)W(CO)_2(Me_2Si{=}CH_2)SiMe_3$,[10b] we suggest that a significantly more stable W–Ge bond is the prime factor. The migration of the Me_3Si group to coordinated $Me_2Ge{=}CH_2$ that occurred in **I** and **III** and migration of Me_3Ge to $Me_2Si{=}CH_2$ in **II** are examples of ligand-stimulated migrations reminiscent of alkyl migrations to coordinated CO that occur during so-called CO insertion reactions.[15]

NMR and GC/MS analysis of the products from the reaction outlined in eq 10 showed the formation of small amounts of $Me_3SiGeMe_3$, identified by comparison of its ^{29}Si NMR resonance (−9.8 ppm) and GC/MS properties with those of an authentic sample. Although the amount formed was small, <5% (we made no attempt to isolate the material), the result is reminiscent of the formation of $Me_3SiSiMe_3$ from photolysis of $(\eta^5\text{-}C_5H_5)_2TiCl(CH_2SiMe_2SiMe_3)$, suggesting that direct homolytic cleavage of the metal–carbon bond occurred in competition with germyl group migration.[10b] The photochemical cleavage of a metal–alkyl bond subsequent to initial loss of CO is a well-established process in cyclopentadienylmetal carbonyl alkyl complexes of this type.[16]

$$(\eta^5\text{-}C_5H_5)W(CO)_3CH_2SiMe_2GeMe_3 \xrightarrow{-CO} (\eta^5\text{-}C_5H_5)W(CO)_2CH_2SiMe_2GeMe_3 \rightarrow [CH_2SiMe_2GeMe_3]^{\bullet} \xrightarrow{\text{solvent}} Me_3SiGeMe_3$$

Experimental Section

Typical syntheses of the new compounds are illustrated below, and spectroscopic and analytical data are presented in Table I. Purifications via column chromatography used silica gel (Malinkrodt) or alumina (Fisher), mesh 60–240; germanium compounds, Me_3GeCl and Me_2GeCl_2, were obtained from Gelest Inc. Mass spectral analysis was obtained using a Hewlett Packard 5890/5971 GC/mass spectrometer with 70-eV ionizing energy.

Synthesis of $ClCH_2SiMe_2GeMe_3$. A solution of $BrCH_2Cl$ (4.27 g, 33.0 mmol) and $ClSiMe_2GeMe_3$[3a] (7.0 g, 33.0 mmol) in 100 mL of THF was placed in a 500-mL round-bottomed flask equipped with a magnetic stirring bar and low-temperature thermometer. To this solution at −78 °C was added slowly (1 h) a hexane solution of 1.6 N *n*-butyllithium (Aldrich Chemical Co., 20.6 mL, 33.0 mmol). The solution was stirred for an additional 20 min and then allowed to warm to room temperature. The solvent was removed and the resulting mixture extracted with 60 mL of hexane. After filtration, fractional distillation yielded $ClCH_2SiMe_2GeMe_3$ (5.2 g, 23 mmol, 70%).

Synthesis of $ICH_2SiMe_2GeMe_3$. Into a 100-mL round-bottomed flask containing a magnetic stirring bar was placed 2.3 g (15.3 mmol) of NaI in 20 mL of acetone. To this solution was added 3.0 g (13.2 mmol) of $ClCH_2SiMe_2GeMe_3$ and the mixture refluxed for 6 h. Subsequent to removal of the acetone by distillation at atmospheric pressure, 60 mL of hexane was added to precipitate sodium salts, which were removed by filtration. The remaining liquid was fractionally distilled to produce 2.5 g (60%) of a light yellow liquid, b.p. 98–100 °C/25 mmHg. The product was used directly. For analytical purposes a second redistillation was performed.

Synthesis of $FpCH_2SiMe_2GeMe_3$. To Fp^-Na^+ (2.2 mmol), obtained from 0.78 g of cyclopentadienyliron dicarbonyl dimer (Strem Chemicals) in 40 mL of THF, was added 1.0 g (4.5 mmol) of $ClCH_2SiMe_2GeMe_3$ in 5 mL of THF at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed, and the resulting product was extracted with 60 mL of hexane. This solution was filtered, concentrated to 5 mL, and chromatographed upon a 2 × 25 cm silica gel column. The yellow band was eluted with hexane. Removal of the solvent yielded $FpCH_2SiMe_2GeMe_3$ (0.6 g, 37%) as an orange oil.

Synthesis of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2SiMe_2GeMe_3$. To a room-temperature solution of $[(\eta^5\text{-}C_5H_5)W(CO)_3]^-Na^+$ (3.9 mmol) in 50 mL of THF was added 2.5 g of $ICH_2SiMe_2GeMe_3$ (7.9 mmol) in 10 mL of THF, and the solution was stirred overnight. Infrared monitoring of the reaction showed the presence of unreacted tungsten carbonylate; therefore the solution was heated to reflux for 2 h. This resulted in the completion of the reaction, and the solvent was removed and the resulting yellowish brown liquid was extracted with 50 mL of hexane. The solution was filtered, concentrated to 5 mL, and placed upon a 2 × 25 cm silica gel column. Using hexane as eluant, a yellow band was developed which yielded 0.9 g (1.7 mmol, 44%) of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2SiMe_2GeMe_3$ after removal of the solvent.

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Synthesis of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2GeMe_2SiMe_3$. A solution of $ICH_2GeMe_2SiMe_3$ (2.5 g, 7.9 mmol) in 10 mL of THF was added to a 50-mL solution of $[(\eta^5\text{-}C_5H_5)W(CO)_3]^-Na^+$ (3.9 mmol). The solution was stirred for 15 h and then refluxed for 2 h. Upon removal of solvent *in vacuo*, the resulting yellow/brown semisolid was extracted with 60 mL of hexane. This solution was filtered, concentrated to 6 mL, placed upon a silica gel column, 2 × 25 cm, and eluted with hexane. The yellow band that formed was collected and shown by NMR to consist of a mixture of $(\eta^5\text{-}C_5H_5)W(CO)_3R$, R = CH_3 and $CH_2GeMe_2SiMe_3$, in the ratio 1:5, respectively. The mixture was placed into a sublimation apparatus and the methyl compound sublimed at 46 °C/0.05 mmHg. The residue, R = $CH_2GeMe_2SiMe_3$, could be purified by crystallization from hexane or sublimed at 65 °C/0.05 mmHg.

Photolysis of $FpCH_2SiMe_2GeMe_3$. A solution of the title compound (0.2 g) dissolved in 1 mL of degassed C_6D_6 in a sealed Pyrex NMR tube, placed 10 cm from a Hanovia 450-W medium-pressure Hg lamp, was irradiated for 30-min periods and the reaction monitored by ^{29}Si NMR spectroscopy. After 3 h no starting material remained, and the solution was placed on a 2.5 × 10 cm silica gel column and eluted with hexane. The yellow band was extracted with hexane and upon removal of the solvent yielded $FpSiMe_2CH_2GeMe_3$ (0.18 g, 90%) as an orange oil.

Photolysis of $FpCH_2GeMe_2SiMe_3$. The title compound (0.15 g) was dissolved in 1 mL of degassed C_6D_6, and the solution was irradiated as above for 20 min in a sealed Pyrex NMR tube. The reaction was monitored by ^{29}Si NMR spectroscopy, and upon disappearance of the starting material the solution was placed upon a 2.5 × 10 cm silica gel column. Elution with hexane developed a yellow band that was collected and upon removal of the solvent yielded $FpGeMe_2CH_2SiMe_3$ (0.12 g, 80%) as an orange oil.

Photolysis of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2GeMe_2SiMe_3$. A sample of 0.2 g of the title complex was irradiated in 1 mL of degassed C_6D_6 in a sealed Pyrex NMR tube. The reaction, monitored by ^{29}Si and ^1H NMR spectroscopy, was complete in 1 h. The solvent was removed, the product dissolved in hexane, and the solution placed upon a 2.5 × 10 cm alumina column and eluted with hexane. The waxy product was sublimed at 50 °C/0.05 mmHg to yield 0.1 g (50%) of $(\eta^5\text{-}C_5H_5)W(CO)_3GeMe_2CH_2SiMe_3$ as a yellow solid.

Photolysis of $WpCH_2SiMe_2GeMe_3$. Irradiation of a 1-mL C_6D_6 solution of $WpCH_2SiMe_2GeMe_3$, 0.10 g (0.19 mmol), in a sealed Pyrex NMR tube was monitored by ^1H and ^{29}Si NMR spectroscopy. After 1 h, the starting material had been consumed and resonances corresponding to $Me_3SiGeMe_3$ and $WpGeMe_3$ were observed. The solvent was removed and the residue recrystallized from hexane to yield 0.06 g (65%) of $WpGeMe_3$. The melting point and other spectral data were in general accord with the literature values except that the IR ν(CO) frequencies (cyclohexane) at 1999, 1923, and 1903 cm^{-1} differed slightly from the literature values reported in cyclohexane: 2010, 1931, and 1908 cm^{-1}.[13]

Thermal treatment of the title complex in refluxing decane resulted in the formation of $WpGeMe_3$ after 1 h. The reaction was monitored via IR spectroscopy, noting the replacement of the bands due to $WpCH_2SiMe_2GeMe_3$ at 2017 and 1926 cm^{-1} by those of $WpGeMe_3$ at 2000, 1924, and 1904 cm^{-1}.

Thermal Reaction of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2SiMe_2GeMe_3$ with *t*-BuOH. A 0.15-g sample of the title complex dissolved in 1 mL of *tert*-butyl alcohol was sealed in a 10-mL Pyrex tube and heated to 150 °C for 15 h. Upon opening of the tube, analysis by GC/MS indicated the presence of several compounds, including $Me_3SiOCMe_3$ in 17% yield. The other materials identified by comparison with authentic samples were WpMe (8%), WpH (5%), $WpGeMe_3$ (22%), and $Me_3GeOCMe_3$ (12%).

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