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with δ 1.348 (X) (t, 6 H, CH_3), 1.355 (X') (t, 6 H, CH_3), 1.689 (A), 1.715 (A'), 1.759 (B), 1.785 (B') (8 H, CH_2), ^2J = 12.82 Hz, ^3J = 7.69 Hz.

1,1,3,3-Tetraphenyl-2-ethyltristibane (11). ^1H NMR (C_6D_6): δ 1.19 (t, 3 H, CH_3), 1.73 (q, 2 H, CH_2) (^3J = 8.0 Hz), 6.9–7.1, 7.5–7.7 (m, C_6H_5).

1,1,4,4-Tetraphenyl-2,3-diethyltetrastibane (12). ^1H NMR (C_6D_6): ABX_3 spin system with δ 1.153 (X) (t, 6 H, CH_3), 1.737 (A), 1.802 (B) (4 H, CH_2), 6.9–7.1, 7.5–7.7 (m, C_6H_5) (^2J = 12.5 Hz, ^3J = 8.0 Hz).

Pentamethyltristibane (13). A mixture of 13.4 g (0.045 mol) of $MeSbBr_2$ and 37.8 g (0.163 mol) of Me_2SbBr is added to 6.6 g (0.27 mol) of Mg filings in 300 mL of THF during 2 h. This produces an exothermic reaction, and the mixture is stirred for 12 h. After evaporation of the solvent, the residue is extracted three times with petroleum ether. Evaporation of the solvent gives 21 g of a mixture of 90 mol % Me_4Sb_2 and 10 mol % 4. Distillation of the mixture gives 18.1 g (73%) of Me_4Sb_2 and a black solid residue. ^1H NMR (C_6D_6): δ 1.00 (s, 6 H, $(CH_3)_2Sb$), 1.01 (s, 9 H, CH_3Sb + $(CH_3)_2Sb$). MS (70 eV, 20 °C) (*m/z*): 440 (M^+), 425 ($M^+ - CH_3$), 410 ($M^+ - 2CH_3$), 395 ($M^+ - 3CH_3$), 365 (Sb_3).

Pentaphenyltristibane (14). Lithium diphenylantimonide was generated by slow addition of 10.6 g (0.03 mol) of Ph_3Sb to a solution of 0.4 g (0.06 mol) of lithium in 150 mL of NH_3 at −80 °C. After the color change, from blue to red, 1.6 g (0.03 mol) of NH_4Cl and 4.0 g (0.015 mol) of $PhSbCl_2$ were added. The solution decolorized, and a brown solid formed. Evaporation of the solvent, washing the solid with water, and drying under reduced pressure gave 8.7 g (77%) of a brown powder containing 14, $(PhSb)_x$, and Ph_4Sb_2. MS (70 eV, 140 °C) (*m/z*): 14, 750 (M^+), 672 ($M^+ - Ph$), 596 ($M^+ - 2\ Ph$); $(PhSb)_x$, 796 (Ph_4Sb_4); Ph_4Sb_2, 552 (M^+). Extraction and crystallization from toluene gave 6.5 g (58%) of Ph_4Sb_2 as yellow crystals. Ph_4Sb_2 was identified by comparison of the NMR spectrum with that of an authentic[22] sample.

Structure Determination of 3. Crystal data as well as details of intensity data collection and refinement are given in Table IV. The density was obtained from neutral buoyancy in aqueous sodium polytungstate solution. The crystal was fixed by gravity and sealed in a glass capillary filled with Ar. The quality and symmetry of the crystal was examined by Weissenberg exposures. Integrated intensities were measured by means of $\omega/2\theta$ scans on a CAD4 diffractometer (Enraf-Nonius).

The structure was solved by a Patterson synthesis (Sb and Si atoms) and completed by Fourier syntheses (C atoms). The refinements were by full matrix (one block only). Hydrogen positions were considered as riding on carbon atoms. The refinement produced good convergence and an even distribution of the variances. Besides several locally written routines, local versions of SHELX-76 and SHELX-86 were used for the calculations, and that of PLUTO-78 was used for Figure 2 (HB-DPS-8/70 equipment at the Zentrum für Datenverarbeitung, Universität Mainz). Table V contains the final parameters.

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Registry No. 1, 73300-46-6; **2a**, 136763-69-4; **2b**, 136763-70-7; **3**, 91043-36-6; **4**, 136763-71-8; **5**, 136763-72-9; **6**, 136763-73-0; **7**, 136782-17-7; **8**, 136763-74-1; **9**, 136763-75-2; **10**, 136763-76-3; **11**, 136763-77-4; **12**, 136763-78-5; **13**, 136763-79-6; **14**, 136763-80-9; $SbBr_3$, 7789-61-9; *i*-Pr_2SbBr, 73300-44-4; $(Me_3Si)_2CHSbCl_2$, 86509-03-7; Me_4Sb_2, 41422-43-9; Et_4Sb_2, 4669-92-5; $MeSbBr_2$, 54553-06-9; Me_2SbBr, 53234-94-9; Ph_3Sb, 603-36-1; Ph_2SbLi, 55085-09-1; $PhSbCl_2$, 5035-52-9; Ph_4Sb_2, 2654-44-6; $(EtSb)_5$, 118399-63-6; $(PrSb)_5$, 118399-67-0; (*t*-$BuSb)_4$, 4791-73-5; $(MesSb)_4$, 118456-82-9; $(EtSb)_x$, 68781-08-8; $(PrSb)_x$, 118399-71-6; $(PhSb)_x$, 136763-81-0.

Supplementary Material Available: Tables listing anisotropic thermal parameters, H atom coordinates, complete bond distances and angles, and torsion angles (5 pages); a table of observed and calculated structure factor amplitudes (60 pages). Ordering information is given on any current masthead page.

UV Photolysis of Digermanyliron Complexes and Dynamic NMR Spectroscopy of Alkoxy-Bridged Bis(germylene)iron Products

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Digermanyliron complexes [$Cp(CO)_2FeGeMe_2GeMe_2R$], with different terminal substituents (R = Me, Et, or OMe) have been synthesized and subjected to UV irradiation. Deoligomerization is observed to occur, initially generating a highly unstable germyl(germylene)iron complex. Where R is alkyl, a germylene is ejected to yield a germyliron complex. Where R is methoxy, internal base stabilization of the germylene moiety by the donor oxygen atom affords a methoxy-bridged bis(germylene)iron complex which is fluxional with a value of $\Delta G^{\ddagger}_{298}$ for the process of germanium–oxygen bond cleavage and germylene rotation of 88.9 kJ mol^{-1}.

Introduction

The coordination chemistry of divalent group 14 species is now well established in the cases of carbenes,[1-3] germylenes,[4-8] and stannylenes.[4-7] In contrast, silylene chemistry is comparatively sparsely reported, due to their lower stability and greater reactivity. Their existence as reactive intermediates or short-lived products is well-known from various reactions with trapping reagents such as 1,3-butadiene and trimethylsilane.[9] Some donor-sta-

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bilized metal complexes[10-16] and very recently a cationic base-free complex[17] have been described.

The photolysis of disilanyl complexes [Cp(CO)$_2$FeSiMe$_2$SiR$_3$] (R = alkyl and/or aryl) gives monosilyl complexes, the key intermediates for which are presumed to be silyl(silylene)iron complexes.[18-22] More recently, we discovered that the photolysis of alkoxy-substituted disilanyliron[11,12] and manganese[13] complexes gives alkoxy-bridged bis(silylene) complexes.

In order to compare the photochemical reactions of the disilanyliron complexes with those of digermanyl complexes, analogous digermanyliron complexes were synthesized and subjected to UV photolysis. Photolysis of the peralkyldigermanyliron complexes afforded mono(germyl)iron complexes, probably via germyl(germylene)iron intermediates, while that of the methoxy-substituted digermanyliron complex gave a methoxy-bridged bis(germylene)iron complex. In the latter, the fluxional process of germylene rotation, a phenomenon also recently reported in the case of some rhenium complexes,[8] has been identified and quantitatively analyzed by line-shape analysis of variable-temperature ^{1}H NMR spectra.

Experimental Section

Methods and Materials. All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled from sodium benzophenone ketyl under nitrogen, immediately prior to use. Na[FeCp(CO)$_2$][23] (Cp = C$_5$H$_5$), Na[FeCp′(CO)$_2$][24] (Cp′ = C$_5$Me$_5$), Me$_3$GeCl,[25] Me$_3$GeGeMe$_2$Cl,[25] and ClMe$_2$GeGeMe$_2$Cl[25] were prepared according to literature methods.

Infrared spectra were recorded using a Jasco IR-810 spectrometer, and ^{1}H NMR spectra were recorded on a continuous-wave Varian EM-390 operating at 90 MHz for monitoring photolysis and on a Bruker AM-600 operating at 600.139 MHz for variable-temperature measurements. ^{13}C NMR spectra were recorded on JEOL FX-90Q and Varian XL-200 spectrometers. NMR measurements were made using C$_6$D$_6$ as solvent, except for the variable-temperature ^{1}H NMR spectroscopy of the methoxy-bridged product obtained upon photolysis of [Cp′(CO)$_2$FeGeMe$_2$GeMe$_2$OMe], for which the solvent was decalin-d_{18}. Mass spectra and high-resolution mass spectra were recorded using JEOL JMS-D300 and JMS-HX110 spectrometers.

[Cp(CO)$_2$FeGeMe$_3$] (1). To a stirring solution of chlorotrimethylgermane (5.0 g, 32.6 mmol) in THF (30 mL) at room temperature was added a solution of Na[FeCp(CO)$_2$] (32.6 mmol) in THF (100 mL) via a cannula. After stirring for 12 h in the dark, the solvent was removed under reduced pressure and the residue extracted with hexane. The extract was filtered through a Celite pad and the filtrate concentrated. The residue was twice purified by Kugelrohr molecular distillation (70–90 °C at 0.08 Torr) to give 1 (7.14 g, 24.2 mmol, 74.3%) as waxy orange crystals. ^{1}H NMR (C$_6$D$_6$): δ 0.57 (9 H, s, CH$_3$), 4.00 (5 H, s, C$_5$H$_5$). ^{13}C NMR (C$_6$D$_6$): δ 6.5 (CH$_3$), 82.7 (C$_5$H$_5$), 216.2 (CO). IR (KBr pellet): ν(CO) 1985 (vs), 1930 cm^{-1} (vs). MS (70 eV): m/z 296 (M$^+$, 36.5%), 225 (100). Anal. Calcd for C$_{10}$H$_{14}$FeGeO$_2$ (mol wt 294.66): C, 32.69; H, 3.70. Found: C, 33.01; H, 3.75.

[Cp(CO)$_2$FeGeMe$_2$GeMe$_3$] (2). To a stirring solution of chloropentamethyldigermane (1.33 g, 5.2 mmol) in THF (5 mL) at room temperature was added a solution of Na[FeCp(CO)$_2$] (5.2 mmol) in THF (15 mL). After stirring for 15 h in the dark, the solvent was removed under reduced pressure and the residue was extracted with hexane. The extract was filtered through a Celite pad and the filtrate concentrated. Molecular distillation of the residue (75–90 °C/0.07 Torr) afforded 2 (0.730 g, 1.8 mmol, 42%) as an orange oil. ^{1}H NMR (C$_6$D$_6$): δ 0.37 (9 H, s, CH$_3$), 0.66 (6 H, s, CH$_3$), 4.10 (5 H, s C$_5$H$_5$). ^{13}C NMR (C$_6$D$_6$): δ 0.5 (CH$_3$), 2.9 (CH$_3$), 82.6 (C$_5$H$_5$), 216.1 (CO). IR (neat): ν(CO) 1990 (vs), 1935 cm^{-1} (vs). MS (70 eV): m/z 400 (M$^+$, 5.5%), 119 (100). Anal. Calcd for C$_{12}$H$_{20}$FeGe$_2$O$_2$ (mol wt 397.3): C, 36.26; H, 5.07. Found: C, 36.23; H, 4.83.

[Cp(CO)$_2$FeGeMe$_2$GeMe$_2$Cl]. In a manner similar to the preparation of [Cp(CO)$_2$FeGeMe$_2$GeMe$_3$], except for using Na[FeCp(CO)$_2$] (24 mmol) and ClMe$_2$GeGeMe$_2$Cl (5.6 g, 20 mmol), [Cp(CO)$_2$FeGeMe$_2$GeMe$_2$Cl] (1.8 g, 4.3 mmol, 22%) was obtained as an orange oil. ^{1}H NMR (C$_6$D$_6$): δ 0.67 (6 H, s, CH$_3$), 0.75 (6 H, s, CH$_3$), 4.22 (5 H, s, C$_5$H$_5$). ^{13}C NMR (C$_6$D$_6$): δ 21.9 (CH$_3$), 24.8 (CH$_3$), 101.9 (C$_5$H$_5$), 234.1 (CO). IR (neat) ν(CO) 1945 (vs), 2010 cm^{-1} (vs). MS (25 eV): m/z 420 (M$^+$, 1.3%), 281 (100). Anal. Calcd for C$_{11}$H$_{17}$ClFeGe$_2$O$_2$ (mol wt 417.7): C, 31.63; H, 4.10. Found: C, 31.93; H, 4.16.

[Cp′(CO)$_2$FeGeMe$_2$GeMe$_2$Cl]. This was prepared analogously to [Cp(CO)$_2$FeGeMe$_2$GeMe$_2$Cl], except for using Na[FeCp′(CO)$_2$]. Yield: 42%. ^{1}H NMR (C$_6$D$_6$): δ 0.78 (6 H, s, CH$_3$), 0.90 (6 H, s, CH$_3$), 1.48 (15 H, s, C$_5$Me$_5$). ^{13}C NMR (C$_6$D$_6$): δ 21.6 (CH$_3$), 25.6 (CH$_3$), 28.9 (C$_5$*Me*$_5$), 114.0 (*C*$_5$Me$_5$), 236.0 (CO). IR (Nujol): ν(CO) 1942 (vs), 1990 cm^{-1} (vs). MS (25 eV): m/z 490 (M$^+$, 0.5%), 351 (100). Anal. Calcd for C$_{16}$H$_{27}$ClFeGe$_2$O$_2$ (mol wt 487.9): C, 39.39; H, 5.58. Found: C, 38.98; H, 5.63.

[Cp(CO)$_2$FeGeMe$_2$GeMe$_2$Et] (3). A solution of EtLi in diethyl ether (0.28 M, 17.8 mL, 5.0 mmol) was added to a solution of [Cp(CO)$_2$FeGeMe$_2$GeMe$_2$Cl] (1.8 g, 4.3 mmol) in diethyl ether (20 mL) at room temperature. After 1.5 h, additional EtLi solution (10 mL, 2.8 mmol) was added to the solution and the mixture was stirred for another 1.5 h. The resulting mixture was filtered to remove the white salt, and the filtrate was concentrated under reduced pressure. Flash chromatography of the residue on silica gel (solvent: hexane) gave crude 3 (800 mg, 1.94 mmol, 45%) which was then purified by preparative GC (SE30, 10%, 1 m). ^{1}H NMR (C$_6$D$_6$): δ 0.34 (6 H, s, CH$_3$), 0.69 (6 H, s, CH$_3$), 0.87–1.14 (5 H, m, C$_2$H$_5$), 4.11 (5 H, s, C$_5$H$_5$). IR (neat): ν(CO) 1988 (vs), 1935 cm^{-1} (vs). MS (70 eV): m/z 414 (M$^+$, 6.2%), 139 (100). Anal. Calcd for C$_{13}$H$_{22}$FeGe$_2$O$_2$ (mol wt 411.3): C, 37.92; H, 5.35. Found: C, 37.58; H, 5.05.

[Cp′(CO)$_2$FeGeMe$_2$GeMe$_2$OMe] (4). To a stirring solution of NaOMe (0.20 g, 8.3 mmol) in MeOH (10 mL) was added solid [Cp′(CO)$_2$FeGeMe$_2$GeMe$_2$Cl] (1.50 g, 5.40 mmol). After stirring for 3 h, the solvent was removed under reduced pressure and the product was extracted with hexane. The extracts were filtered through a Celite pad, concentrated, and purified by Kugelrohr molecular distillation at 90–110 °C/0.08 Torr to give 4 as waxy orange crystals (1.34 g, 2.8 mmol, 51%). ^{1}H NMR: (C$_6$D$_6$) δ 0.63 (6 H, s, GeCH$_3$), 0.75 (6 H, s, GeCH$_3$), 1.61 (15 H, s, C$_5$Me$_5$), 3.60 (3 H, s, OCH$_3$); (decalin-d_{18}) δ 0.43 (6 H, s, GeCH$_3$), 0.48 (6 H, s, GeCH$_3$), 1.85 (15 H, s, C$_5$Me$_5$), 3.38 (3 H, s, OMe). ^{13}C NMR (C$_6$D$_6$): δ 1.0 (GeCH$_3$), 2.7 (GeCH$_3$), 9.9 (C$_5$*Me*$_5$), 52.5 (OCH$_3$), 95.0 (*C*$_5$Me$_5$), 217.7 (CO). IR (neat): ν(CO) 1975 (vs), 1922 cm^{-1} (vs). MS (13.5 eV): m/z 458 (M$^+$, 26.9%), 351 (100). Anal. Calcd for C$_{17}$H$_{30}$FeGe$_2$O$_3$ (mol wt 483.4): C, 42.62; H, 6.16. Found: C, 42.83; H, 6.25.

[Cp(CO)$_2$FeGeMe$_2$Et] (5). Synthesized photochemically; see section "Photolysis". ^{1}H NMR (C$_6$D$_6$): δ 0.53 (6 H, s, CH$_3$),

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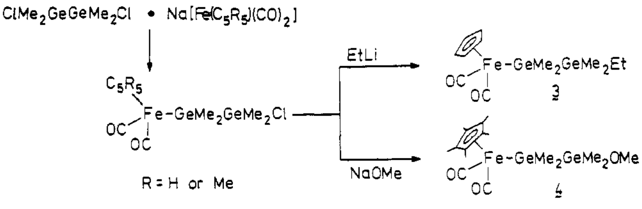
0.99–1.55 (5 H, m, C_2H_5), 4.04 (5 H, s, C_5H_5). IR (neat): ν(CO) 1988 (vs), 1935 cm^{-1} (vs). MS (70 eV): m/z 310 (M^+, 9.5%), 139 (100). Anal. Calcd for $C_{11}H_{16}O_2FeGe$ (mol wt 308.7): C, 34.64; H, 4.23. Found: C, 35.55; H, 4.28.

[Cp′(CO)Fe{GeMe$_2$- -O(Me)- -GeMe$_2$}] (6). Synthesized photochemically; see section "Photolysis". ^{1}H NMR (C_6D_6): δ 0.71 (6 H, s, CH_3), 0.76 (6 H, s, CH_3), 1.75 (15 H, s, C_5Me_5), 2.84 (3 H, s, OCH_3), 0.52 (6 H, s, $GeCH_3$), 0.68 (6 H, s, $GeCH_3$), 1.80 (15 H, s, C_5Me_5), 3.10 (3 H, s, OMe). ^{13}C NMR: δ 8.4 (CH_3), 10.4 (CH_3), 11.7 ($C_5\mathit{Me}_5$), 50.3 (OCH_3), 88.9 (C_5Me_5), 221.3 (CO). IR (hexane): ν(CO) 1880 cm^{-1} (vs). MS (70 eV): m/z 458 (M^+, base peak). Exact Mass Calcd for $C_{16}H_{30}FeGe_2O_2$: 458.0019. Found: 458.0022.

Photolysis of [Cp(CO)$_2$FeGeMe$_2$GeMe$_2$R] (R = Me, Et, or OMe). [Cp(CO)$_2$FeGeMe$_2$GeMe$_2$R] was placed in a Pyrex NMR tube (o.d. 5 mm) and dissolved in deoxygenated C_6D_6. The tube was then immersed in an ice–water bath and irradiated with a 450-W medium-pressure Hg lamp (Ushio UV-450) placed in a water-cooled quartz jacket. After 5-min irradiation, the color of the solution changed from orange to brown. For R = Me or Et, identification of products was accomplished by comparing their retention times on GC and the patterns of their GC–MS spectra with those of authentic samples, except for [Cp(CO)$_2$FeGeMe$_2$Et] (5), which was isolated from the reaction mixture by preparative GC. Yields of products were determined by gas chromatography with dodecane as internal standard and calculated for the consumed starting materials.

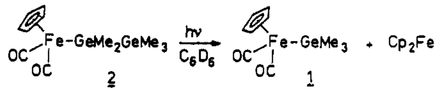
Results and Discussion

Synthesis. The permethylated germyl- and digermanyliron complexes were prepared by reaction of chlorogermane and chlorodigermane with Na[Fe(C_5R_5)(CO)$_2$] (R = H or Me), elimination of the salt, and purification by molecular distillation. The ethyl- and methoxy-substituted digermanyliron complexes were synthesized by reaction of 1,2-dichlorodigermane with the complex anion to form a digermanyliron complex with a terminal chlorine and then reaction of this with either ethyl lithium or sodium methoxide, as shown in eq 1.



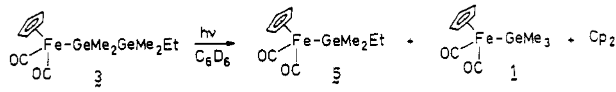
(1)

Photochemistry of [FpGeMe$_2$GeMe$_2$R] (R = Me and Et). Photolysis was performed on samples in NMR tubes sealed under vacuum and monitored by ^{1}H NMR spectroscopy. Irradiation of [FpGeMe$_2$GeMe$_3$] (2) for 5 min (42% conversion) afforded [FpGeMe$_3$] (1) and ferrocene in 87 and 6% yields, respectively (eq 2). When the photolysis was performed in the presence of 2,3-dimethyl-1,3-butadiene, a germylene trapping agent,[26] the formation of 1 and ferrocene was observed, but the germylene-trapped product, 1,1,3,4-tetramethyl-1-germacyclopent-3-ene, was not detected. This result is analogous to the absence of trapped silylene intermediate during the photolysis of disilanyliron complexes.[18,22]



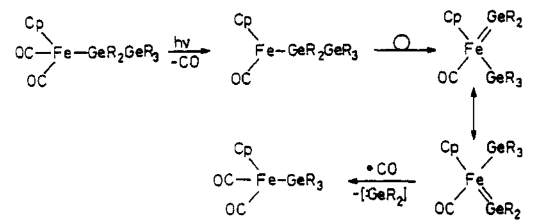
(2)

Irradiation of [FpGeMe$_2$GeMe$_2$Et] (3) for 5 min (77% conversion) afforded 1, 5, and ferrocene in 31, 62, and 5% yields, respectively (eq 3). This alkyl scrambling shows that alkyl migration occurs between the two germanium atoms during photolysis and that a germylene (either GeMeEt or GeMe$_2$) is expelled. This is consistent with the photochemical deoligomerization mechanism shown in Scheme I, in which the first step is envisaged as photolytic ejection of a carbonyl group to give a 16-electron intermediate which rearranges to give a germyl(germylene)iron complex. 1,3-Alkyl exchange may then occur, followed by carbonyl recombination and germylene expulsion. Fair agreement of the experimental product ratio of 1 to 5 (1:2) with the theoretically expected ratio of 2:3 further supports this mechanism, which is analogous to that of the silicon analogue.



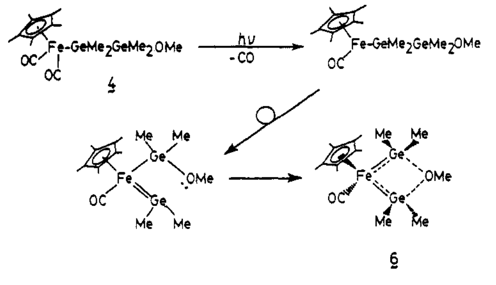
(3)

Scheme I. Photolytic Deoligomerization Mechanism



Photochemistry of [Fp′GeMe$_2$GeMe$_2$OMe] (4) and Structure of Product. In this case, the photochemical reaction proceeds more cleanly, no ferrocene formation being observed. Infrared spectroscopy of the product of photolysis of the methoxy–digermanyl complex indicated that only one carbonyl group remained, and at a significantly lower wavenumber (1880 cm^{-1}) than that in the photolysis precursor (1975, 1922 cm^{-1}), indicating greater ability of the metal to back-donate electron density to the carbonyl carbon atom.

^{1}H NMR spectroscopic monitoring during photolysis in decalin-d_{18} indicated that the methoxy signal underwent a high-field shift of 0.28 ppm. The two prephotolysis germyl methyl peaks (0.43 and 0.48 ppm) disappeared, giving rise to two other peaks at slightly lower field (0.52 and 0.68 ppm). These observations are consistent with a similar photolysis mechanism to that described above for the peralkyldigermanyl complexes, except that the germyl(germylene) intermediate is stabilized by the methoxy group, which is considered to bridge both germanium moieties and inhibits the expulsion of germylene, as shown in eq 4. This gives rise to a bis(germylene)iron complex containing an Fe–Ge–O–Ge ring and parallels the observations for the photolysis of the (methoxydisilanyl)iron complexes.[11,12]



6

(4)

Fluxionality and Variable-Temperature NMR Studies of [Cp′(CO)Fe{GeMe$_2$- -O(Me)- -GeMe$_2$}] (6). The room-temperature ^{1}H NMR spectrum of [Cp′(CO)Fe{GeMe$_2$- -O(Me)- -GeMe$_2$}] (6), the product obtained

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(26) Massol, M.; Satgé, J.; Rivière, P.; Barrau, J. *J. Organomet. Chem.* **1970**, *22*, 599.

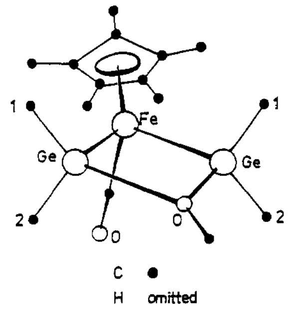
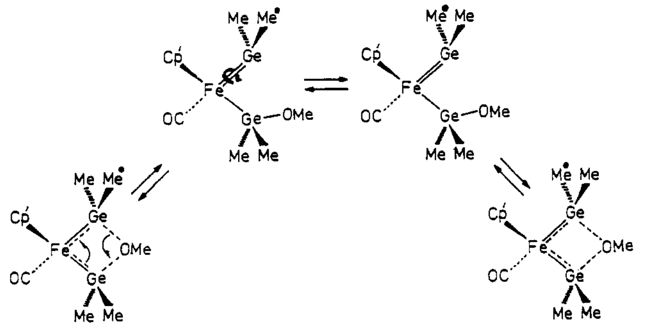


Figure 1. Drawing to show stereochemistry of $[Cp'(CO)Fe\{GeMe_2{-}{-}O(Me){-}{-}GeMe_2\}]$ (6). Methyl groups 1 and 2 undergo mutual exchange.

Scheme II. Mechanism of Germylene Rotation



upon photolysis of $[Fp'GeMe_2GeMe_2OMe]$ (4), showed two germanium methyl peaks, consistent with the proposed structure, due to the different environments above and below the Fe–Ge–O–Ge plane. As the temperature was raised, however, the peaks gradually broadened, coalesced (142 °C), and became a singlet, sharp at temperatures above 170 °C. This averaging of magnetic environments on the NMR time scale at high temperature indicates that the germanium methyl groups (see Figure 1; exchanging methyl groups are labeled 1 and 2) are undergoing mutual exchange. An exchange mechanism accounting for this is given in Scheme II and involves firstly cleavage of one Ge--O partial bond, rotation of the resulting germylene moiety about the Fe=Ge double bond to interchange the methyl group environments, and finally recombination of the Ge--O partial bond. Using the program DNMR3,[27] computer-generated spectra were obtained and visually fitted to the experimentally obtained spectra in order to evaluate the rate constants for the exchange process at the different temperatures (see Figure 2). Graphic application of the Eyring equation (see Figure 3) to the kinetic data so obtained gave the thermodynamic parameters, $\Delta H^{\ddagger}$ = 95.3 ± 2.6 kJ mol^{-1}, $\Delta S^{\ddagger}$ = 21.4 ± 6.2 J K^{-1} mol^{-1}, and $\Delta G^{\ddagger}_{298}$ = 88.9 ± 4.4 kJ mol^{-1} (calculated for a fluxional cycle comprising rotation of both germylenes). The small value of the entropy term indicates that the exchange is intramolecular. The physical significance of the enthalpy and Gibb's free energy terms is more difficult to ascertain: $\Delta H^{\ddagger}$ is perhaps best regarded as an indication of the Ge--O partial bond strength, and $\Delta G^{\ddagger}$ the difference between the ground-state and transition-state energies. The transition-state geometry may be regarded as a germyl(germylene) complex with the germylene methyl groups coplanar with the iron and germanium atoms. For certain coordinated carbenes, both theoretical[28] and experimental[3] studies on the $[Cp(CO)_2M{=}CR_2]^+$ system indicate that there are two possible orientations for the carbene moiety: either such that the CR_2 ligand coincides with the symmetry plane of the molecule or is perpendicular to this. In the case of $[Cp(Ph_2PCH_2CH_2PPh_2)Fe{=}CH_2]^+$,[3] the experimentally determined rotational energy barrier, $\Delta G^{\ddagger}$, is 43.5 ± 4.2 kJ mol^{-1}, while the theoretically determined energy difference between the two carbene orientations in $[Cp(CO)_2Fe{=}CH_2]^+$ [28] is 26 kJ mol^{-1}. The ground-state geometry in the present germylene complex, however, is more debatable, depending upon the relative energies of the two steps (Ge--O partial bond cleavage and germylene rotation) and upon which is regarded as the rate-determining step. Further work is in progress to clarify this aspect.

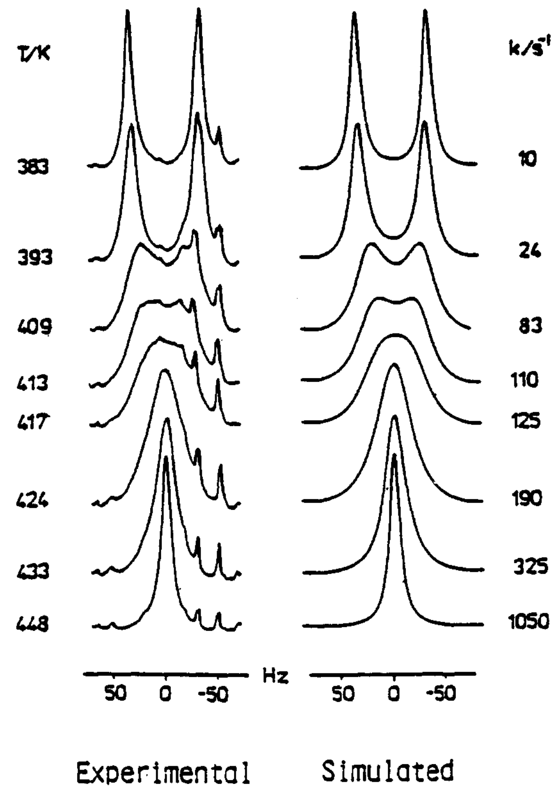


Figure 2. Experimental and computer-synthesized variable-temperature ^1H NMR spectra and rate constants, k, for germylene rotation in $[Cp'(CO)Fe\{GeMe_2{-}{-}O(Me){-}{-}GeMe_2\}]$ (6).

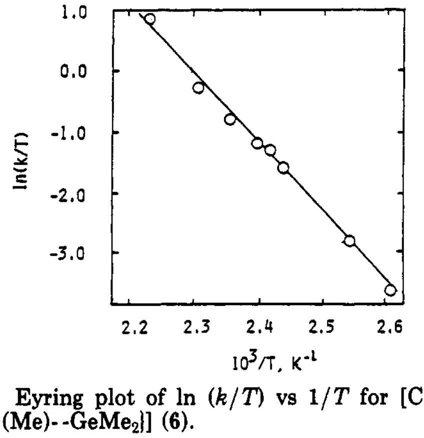


Figure 3. Eyring plot of ln (k/T) vs $1/T$ for $[Cp'(CO)Fe\{GeMe_2{-}{-}O(Me){-}{-}GeMe_2\}]$ (6).

Thus, the photochemistry of the digermanyliron complexes is similar to that of the disilanyl complexes. However, whereas for the methoxy-bridged bis(silylene) com-

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(27) Binsch, G.; Kleier, D. A. *DNMR3*; Program 165; Quantum Chemistry Program Exchange: Indiana University, Bloomington, IN, 1070.

(28) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585.

plexes,[11,12] no silylene rotation was observed,[29] rotation of the germylene moiety in analogous germanium complexes has been observed and quantitatively analyzed. This difference reflects both the greater stability of M = ER_2 when E is Ge as opposed to Si[6,30] and the weaker nature of the Ge–O as compared with the Si–O bond.

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Registry No. 1, 32054-63-0; 2, 137364-17-1; 3, 137364-18-2; 4, 137364-19-3; 5, 137364-20-6; 6, 137364-21-7; [Cp-$(CO)_2FeGeMe_2GeMe_2Cl$], 137364-22-8; [Cp′-$(CO)_2FeGeMe_2GeMe_2Cl$], 137364-23-9; $ClGeMe_3$, 1529-47-1; Na-[$FeCp(CO)_2$], 12152-20-4; $ClMe_2GeGeMe_3$, 22640-93-3; $ClMe_2GeGeMe_2Cl$, 22702-77-8; Na[$FeCp'(CO)_2$], 52409-74-2.

Supplementary Material Available: Figures of ^1H NMR spectra of 6 and 4 (2 pages). Ordering information is given on any current masthead page.

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[29] Ueno, K.; Ogino, H. Unpublished result.

[30] Pannell, K. H. Private communication.

New Pathways for Reactions of Transition-Metal–Propargyl Complexes with $Fe_2(CO)_9$. Characterization of Products Derived from Iron and Chromium Propargyls

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Reactions of the isoelectronic metal–propargyl complexes $Cp(CO)_2FeCH_2C{\equiv}CPh$ (**1**) and $Cp(NO)_2CrCH_2C{\equiv}CPh$ (**2**) with $Fe_2(CO)_9$ were investigated. In pentane at room temperature **1** affords a binuclear metal–η^4-allylcarbonyl product, $(CO)_3Fe[\eta^4\text{-}C(O)C(Ph)\cdots C(Fe(CO)_2Cp)\cdots CH_2]$ (**3**), whereas in hexane, also at room temperature, **2** surprisingly yields a homobinuclear metal–μ-η^2,η^3-allenyl product, $(CO)_3Fe(\mu\text{-}\eta^2,\eta^3\text{-}PhC{=}C{=}CH_2)Fe(CO)_2(NO)$ (**4**), and known $CpCr(CO)_2(NO)$. A mechanism for the formation of **3** is proposed which is similar to that for the cycloaddition reactions of metal–propargyl complexes with neutral electrophiles. Complex **4** arises by an unprecedented complete transfer of the propargyl group as the corresponding allenyl ligand from the parent transition metal (Cr) to the substrate metal (Fe). The diyne $(PhC{\equiv}CCH_2)_2$ (**5**), which forms in the preparation of **1** and **2**, reacts with $Fe_2(CO)_9$ to give a new bicyclic ferrole complex, $(CO)_6Fe_2[PhC{=}C(C_2H_4)C{=}CPh]$ (**6**). Complexes **3**, **4**, and **6** were characterized by a combination of elemental analysis, mass spectrometry, and IR and ^1H and ^{13}C NMR spectroscopy; the structures of **3** and **6** were determined by single-crystal X-ray analysis. Crystallographic parameters: **3** $P\bar{1}$, $a = 8.967$ (2) Å, $b = 9.304$ (3) Å, $c = 12.533$ (4) Å, $\alpha = 98.02$ (3)°, $\beta = 104.84$ (2)°, $\gamma = 105.48$ (3)°, $Z = 2$, $R = 0.032$, $R_w = 0.032$ for 4121 independent reflections with $I > 3\sigma(I)$; **6** $P\bar{1}$, $a = 7.895$ (1) Å, $b = 9.056$ (1) Å, $c = 15.722$ (2) Å, $\alpha = 78.27$ (1)°, $\beta = 79.84$ (1)°, $\gamma = 77.12$ (1)°, $Z = 2$, $R = 0.028$, $R_w = 0.028$ for 3784 independent reflections with $I > 3\sigma(I)$.

Introduction

The reactions of transition-metal–propargyl complexes $L_nMCH_2C{\equiv}CR$ (L_nM = $Cp(CO)_3Mo$ and -W, $Cp(CO)_2Ru$) with metal carbonyls have recently been used for the convenient synthesis of heterobinuclear and -trinuclear metal compounds with a variety of bridging hydrocarbyl ligands,[1-4] especially allenyls.[2,3,5] In particular, diverse products have been obtained with $Fe_2(CO)_9$ which depend on the identity of L_nM. To further elucidate the effect of L_nM on these reactions, the behavior of the isoelectronic (formally d^6) transition-metal–propargyl compounds $Cp(CO)_2FeCH_2C{\equiv}CPh$ (**1**) and $Cp(NO)_2CrCH_2C{\equiv}CPh$ (**2**) toward $Fe_2(CO)_9$ was investigated. Portions of this work have been previously communicated.[3]

Experimental Section

General Procedures and Measurements. All reactions and manipulations of air-sensitive compounds were conducted under

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