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Hydrolysis of *tert*-Butyl and Phenyl Ferrocenyldichlorogermanes: Characterization of Di-*tert*-butyldiferrocenyldigermoxanediol and 1,3,5-Triphenyl-1,3,5-triferrocenylcyclotrigermoxane

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The hydrolysis of ferrocenyl-*tert*-butyldichlorogermane (Fc(*t*-Bu)GeCl$_2$, **1a**, Fc = (η^5-C$_5$H$_5$)-Fe(η^5-C$_5$H$_4$)) resulted in the formation of the digermoxanediol [Fc(*t*-Bu)(HO)Ge]$_2$O (**2**), which in the solid state forms intermolecularly hydrogen-bonded dimeric **2a** or double-chain **2b**, structures dependent upon the solvent used for recrystallization. By contrast, similar hydrolysis of ferrocenylphenyldichlorogermane (FcPhGeCl$_2$, **1b**) led to the formation of the cis and trans isomers of (FcPhGeO)$_3$ (**3a** and **3b**) as a 1:4 ratio mixture, respectively. The cis isomer, **3a**, can be converted to the thermodynamically more stable trans isomer, **3b**. The molecular structures of **2a**, **2b**, **3a**, and **3b** have been determined by X-ray diffraction analysis.

Introduction

Transition-metal-containing organosilicon materials are an active research aspect of silicon chemistry.[1] Such systems include the family of ferrocenyl derivatives including siloxanes,[2] alkoxysilanes,[3] polysilanes,[4] and silylene ferrocenylene polymers.[5] Interest in these materials stems from the incorporation of many unusual properties such as the reversible redox behavior, permeability, thermal and photochemical stability, and unusual structural features introduced by the ferrocenyl groups.

We recently reported the synthesis of ferrocenylsilanediol materials containing a number of organic substituents, Fc(R)Si(OH)$_2$,[6] Fc = (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$), and the Manners group has reported diferrocenylsilanediol, Fc$_2$Si(OH)$_2$, and tetraferrocenyldisiloxanediol, [Fc$_2$(HO)Si]$_2$O.[7] In general, despite the large array of silanols reported,[8] few analogous organogermanols have been reported, possibly because of their higher sensitivity toward self-condensation.[9] Furthermore, transition-metal derivatives of germanium are a much less developed field of chemistry than that of Si.[10] We now report that the hydrolysis of two ferrocenyldichlorogermanes, Fc(R)GeCl$_2$, R = *t*-Bu (**1a**), Ph (**1b**), leads to the formation of new ferrocenyl-containing materials, a

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digermoxanediol, [Fc(*t*-Bu)(HO)Ge]$_2$O, **2**, and two isomeric cyclotrigermoxanes, (FcPhGeO)$_3$, **3a** (cis) and **3b** (trans). We also report their single-crystal X-ray diffraction analyses which in the case of **2** illustrate interesting supramolecular self-assemblies dependent upon the solvent of recrystallization.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere or under high vacuum. Tetrahydrofuran was distilled under a nitrogen atmosphere from sodium benzophenone ketyl prior to use. The following reagents were used as received from the suppliers named, silica gel (grade 62, 60−200 mesh), tetramethylethylenediamine (TMEDA), ferrocene, 1.0 M HCl solution in ether, and 1.6 M *n*-butyllithium in hexanes, Aldrich; PhGeCl$_3$, *t*-BuGeCl$_3$, Gelest. TMEDA was dried with calcium oxide and distilled prior to use. Other reagents were synthesized by literature procedures: [1]-*tert*-butylchlorogermyleneferrocenophane,[11] ferrocenylphenyldichlorogermane.[11] Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-300 Fourier transform spectrometer; infrared (IR) spectra were obtained with use of CCl$_4$ as solvent and as KBr disk on a Perkin-Elmer 1600 series FT-IR spectrometer; elemental analyses were performed by Galbraith Laboratories.

Synthesis of *tert*-Butyldichloroferrocenylgermane (1a). To a solution of [1]-*tert*-butylchlorogermaneferrocenophane (5.0 g, 143 mmol) in 100 mL of hexane was added dropwise at 0 °C 14.3 mL of a 1.0 M HCl in ether solution. After complete addition the solution was stirred for 1 h and filtered. The solvent was removed under vacuum to yield 4.40 g (80%) of the yellow powder product Fc(*t*-Bu)GeCl$_2$ (**1a**). Mp 58−60 °C. ^{1}H NMR (C$_6$D$_6$) δ 1.05 (s, 9H, C(CH$_3$)$_3$), 4.09, 4.18 (s, s, 2H, 7H, Cp). ^{13}C NMR (C$_6$D$_6$) δ 25.38 (C(*C*H$_3$)$_3$), 35.01 (*C*(CH$_3$)$_3$), 70.01 (η^5-C$_5$H$_5$), 70.51 (*ipso*-C), 71.66, 72.84 (η^5-C$_5$H$_4$). Anal. Calcd for C$_{14}$H$_{18}$Cl$_2$FeGe: C, 44.60; H, 4.70. Found: C, 45.13; H, 4.83.

Synthesis of 1,3-Di-*tert*-butyl-1,3-diferrocenyldigermanoxanediol (2). To a solution of H$_2$O (0.26 g, 13.6 mmol) and Et$_3$N (1.26 g, 12.5 mmol) in 30 mL of ether and 5 mL of acetone was added dropwise a 30-mL diethyl ether solution of Fc(*t*-Bu)GeCl$_2$ (2.20 g, 5.7 mmol). During the addition precipitation of Et$_3$N·HCl was observed. After complete addition the mixture was further stirred for 1 h and then concentrated to approximately one-tenth of the original volume. Thirty milliliters of hexane was added to promote complete salt precipitation, and the resulting mixture was filtered to remove the hydrogen chloride salts. The solvent was removed under vacuum to yield 1.80 g (93%) of the yellow solid product, [Fc(*t*-Bu)(HO)Ge]$_2$O (**2**). ^{1}H NMR (C$_6$D$_6$) δ 1.36 (s, 18H, C(CH$_3$)$_3$), 2.41 (s, 2H, Ge−OH), 4.17−4.20 (m, 16H, Cp), 4.49 (s, 2H, Cp). ^{13}C NMR (C$_6$D$_6$) δ 27.21 (C(*C*H$_3$)$_3$), 28.12 (*C*(CH$_3$)$_3$), 69.19 (η^5-C$_5$H$_5$), 70.20 (*ipso*-C), 70.64, 70.93, 73.17, 73.36 (η^5-C$_5$H$_4$). Anal. Calcd for C$_{28}$H$_{38}$Fe$_2$Ge$_2$O$_3$: C, 49.49; H, 5.64. Found: C, 50.12; H, 5.93. IR (cm^{-1}) ν_{OH} (CCl$_4$) 3645 (s), 3518 (br, w); ν_{OH} (KBr) 3361 cm^{-1} (br, s); ν_{GeOGe} (KBr) 838 cm^{-1}. Recrystallization from benzene yielded **2a** (mp 146−148 °C); recrystallization from a benzene/THF (1:2) mixture yielded **2b** (mp 150−151 °C).

Synthesis of *cis*- and *trans*-1,3,5-Triphenyl-1,3,5-triferrocenylcyclo trigermanoxane (3a and 3b). Treatment of FcPhGeCl$_2$ as described above (1.0 g, 2.5 mmol) afforded 0.82 g of the yellow solid product. The ^{1}H and ^{13}C NMR spectra of the product showed a mixture of the cis and trans isomers in the ratio of 1:4 (**3a**:**3b**). Recrystallization of the mixture from a CH$_2$Cl$_2$/hexane solution gave orange single crystals of **3a**, *cis*-(FcPhGeO)$_3$, mp 170−172 °C. ^{1}H NMR (C$_6$D$_6$) δ 4.14 (s, 15H, η^5-C$_5$H$_5$), 4.25, 4.53 (t, t, J = 1.7 Hz, 6H, 6H, η^5-C$_5$H$_4$), 7.10−7.12 (m, 9H, Ph), 7.92−7.94 (m, 6H, Ph). ^{13}C NMR (C$_6$D$_6$) δ 69.32 (η^5-C$_5$H$_5$), 70.72 (*ipso*-C), 71.26, 73.31 (η^5-C$_5$H$_4$), 128.40, 130.07, 133.49, 138.49 (Ph). Anal. Calcd for C$_{48}$H$_{42}$Fe$_3$Ge$_3$O$_3$: C, 54.79; H, 4.02. Found: C, 54.85; H, 4.22.

The trans isomer **3b** could not be separated from the mixture of **3a** and **3b** by recrystallization or column chromatography. However, the pure trans isomer **3b** could be obtained by the following procedure. A 100-mL round-bottom flask was charged with a mixture of **3a** and **3b** (100 mg) in 15 mL of 95% ethanol. The flask was then heated to reflux. Four drops of 4 M NaOH(aq) solution was added and the solution was further refluxed for 2 h. After the mixture was cooled to room temperature, a yellow powder began to precipitate. The mixture was further cooled to −15 °C overnight and then filtered. After the filtrate was dried under vacuum 80 mg of the pure *t*-(FcPhGeO)$_3$ (**3b**) was isolated, mp 212−4 °C. ^{1}H NMR (C$_6$D$_6$) δ 3.99−4.06 (m, 2H, η^5-C$_5$H$_4$), 4.07 (s, 5H, η^5-C$_5$H$_5$), 4.11 (s, 10H, η^5-C$_5$H$_5$), 4.15−4.17 (m, 6H, η^5-C$_5$H$_4$), 4.33, 4.36 (q, q, J = 1.53 Hz, J = 1.59 Hz, 2H, 2H, η^5-C$_5$H$_4$), 7.05−7.27 (m, 9H, Ph), 8.04−8.06 (m, 4H, Ph), 8.17−8.20 (m, 2H, Ph); ^{1}H NMR (CDCl$_3$) δ 3.96 (m, 2H, η^5-C$_5$H$_4$), 3.99 (s, 5H, η^5-C$_5$H$_5$), 4.03 (s, 10H, η^5-C$_5$H$_5$), 4.13 (m, 4H, η^5-C$_5$H$_4$), 4.17 (m, 2H, η^5-C$_5$H$_4$), 4.25 (m, 4H, η^5-C$_5$H$_4$), 7.22−7.47 (m, 9H, Ph), 7.75−7.78 (m, 4H, Ph), 7.89−7.91 (m, 2H, Ph). ^{13}C NMR (C$_6$D$_6$) δ 69.16, 69.23 (η^5-C$_5$H$_5$), 70.44 (*ipso*-C), 70.62 (*ipso*-C), 71.06, 71.17, 71.24, 73.07, 73.19, 73.23 (η^5-C$_5$H$_4$), 128.53, 128.64, 130.28, 130.45, 133.64, 133.75, 138.73, 138.90 (Ph); ^{13}C NMR (CDCl$_3$) δ 68.67, 68.74 (η^5-C$_5$H$_5$), 69.81 (*ipso*-C), 69.91 (*ipso*-C), 70.59, 70.73, 72.60, 72.68, 72.78 (η^5-C$_5$H$_4$), 128.12, 128.27, 129.94, 130.13, 133.18, 133.28, 137.89, 138.09 (Ph). Anal. Calcd for C$_{48}$H$_{42}$Fe$_3$Ge$_3$O$_3$: C, 54.79; H, 4.02. Found: C, 54.21; H, 4.36. IR (ν_{GeOGe}, KBr, cm^{-1}) 841.

X-ray Diffraction Studies. Crystals (**2a**, **2b**, **3a**, and **3b**) suitable for X-ray diffraction analysis were obtained from different solvents: benzene (**2a**), THF and benzene (**2b**), and CH$_2$Cl$_2$/hexane (**3a** and **3b**). Intensity data were collected on a Nicolet−Siemens R3m/V four-circle diffractometer at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Unit cell parameters and standard deviations were obtained by least-squares fit of 25 reflections randomly distributed in reciprocal space in the 2θ range of 15−30°. The ω-scan technique was applied in the 2θ range 3.5° ≤ 2θ ≤ 50.0° with variable scan speeds except for the complexes **2b** and **3b** (4.2° ≤ 2θ ≤ 50.0°). A semiempirical absorption correction was applied to both data sets, giving a min/max transmission ratio of 0.188/0.245 for **2a** and 0.024/0.049 for **2b**. No absorption correction was applied in the cases of **3a** and **3b**. For **3b**, the disorder for the phenyl group on the Ge3 atom was observed. All structures were solved by direct methods and refined by using the PC-version of the SHELEXTL PLUS crystallographic software supplied by Siemens. Full-matrix least-squares refinement minimizing $\sum w(F_o - F_c)^2$ was carried out with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms not attached to oxygen were placed at calculated positions (C−H = 0.96 Å; UH = 0.08) during refinements, and those for the hydroxyl groups were located on a difference map. The weighing scheme has the form $w^{-1} = \sigma^2(F) + gF^2$, and the final R factors the form $R = \sum w|F_o - F_c|/\sum F_o$ and $R_w = [w|F_o - F_c|^2/\sum wF_o^2]^{1/2}$. Crystallographic data are summarized in Table 1, and selected bond lengths and angles are provided in Table 2, 3, and 4.

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Table 1. Crystallographic Data for 2a, 2b, 3a, and 3b

	2a	2b	3a	3b
empirical formula	$C_{28}H_{38}Fe_2Ge_2O_3$	$C_{28}H_{38}Fe_2Ge_2O_3$	$C_{48}H_{42}Fe_3Ge_3O_3$	$C_{48}H_{42}Fe_3Ge_3O_3$
fw	679.46	679.46	1052.14	1052.14
cryst size (mm^3)	0.32 × 0.30 × 0.24	0.80 × 0.44 × 0.28	0.60 × 0.36 × 0.18	0.30 × 0.28 × 0.14
group system	triclinic	monoclinic	monoclinic	triclinic
crystal space	$P\bar{1}$	$C2/c$	$P2_1/n$	$P\bar{1}$
unit cell dimens				
a (Å)	10.315(4)	39.068(12)	14.344(4)	11.713(2)
b (Å)	12.270(4)	15.137(4)	18.053(6)	12.128(2)
c (Å)	12.641(4)	10.674(3)	16.013(3)	16.639(3)
α, deg	92.54(3)	90	90	89.880(10)
β, deg	113.02(3)	97.41(2)	97.14(2)	75.550(10)
γ, deg	100.09(3)	90	90	66.350(10)
V (Å^3)	1438.4(9)	6260(3)	4217(2)	2083.8(6)
Z	2	8	4	2
d_{calc} (g·cm^{-1})	1.569	1.442	1.657	1.677
μ, cm^{-1}	30.84	28.35	31.57	31.95
2θ range (deg)	3.52−50.1	4.20−50.1	3.62−50.1	4.08−50.1
index ranges				
h	0 to 12	0 to 46	−17 to 0	0 to 13
k	−14 to 14	0 to 18	0 to 22	−13 to 14
l	−15 to 13	−12 to 12	−18 to 19	−19 to 19
no. of reflns collected	5346	5610	7661	7771
no. of indep reflns/R_{int}	5043/0.0578	5610/0.0143	7356/0.0713	7376/0.0248
no. of params	316	318	515	514
final R indices ($I > 2.0\sigma(I)$)	$R = 0.0345$, $R_w = 0.0773$	$R = 0.0516$, $R_w = 0.1433$	$R = 0.0567$, $R_w = 0.1156$	$R = 0.0467$, $R_w = 0.0922$
R indices (all data)	$R = 0.0485$ $R_w = 0.0838$	$R = 0.0680$ $R_w = 0.1556$	$R = 0.1193$ $R_w = 0.1410$	$R = 0.0858$ $R_w = 0.1079$
goodness of fit	1.021	1.045	1.000	1.001
largest diff peak/hole, e/Å^3	0.520/−0.568	1.154/−0.951	0.888/−0.604	0.504/−0.422

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2a and 2b

2a		2b	
bond length (Å)			
Ge(1)−O(2)	1.774(3)	Ge(1)−O(2)	1.762(3)
Ge(1)−O(1)	1.786(3)	Ge(1)−O(1)	1.791(4)
Ge(2)−O(2)	1.768(2)	Ge(2)−O(2)	1.769(3)
Ge(2)−O(3)	1.781(3)	Ge(2)−O(3)	1.779(4)
Ge(1)−C(1)	1.924(4)	Ge(1)−C(1)	1.928(5)
Ge(2)−C(19)	1.924(4)	Ge(2)−C(19)	1.937(6)
Ge(1)−C(11)	1.972(5)	Ge(1)−C(11)	1.977(6)
Ge(2)−C(15)	1.962(4)	Ge(2)−C(15)	1.960(6)
bond angles (deg)			
O(2)−Ge(1)−O(1)	106.16(13)	O(2)−Ge(1)−O(1)	107.23(18)
O(2)−Ge(2)−O(3)	106.59(13)	O(2)−Ge(2)−O(3)	101.87(18)
O(2)−Ge(1)−C(1)	111.56(14)	O(2)−Ge(1)−C(1)	107.8(2)
O(2)−Ge(1)−C(11)	106.25(15)	O(2)−Ge(1)−C(11)	105.2(2)
O(1)−Ge(1)−C(1)	103.69(14)	O(1)−Ge(1)−C(1)	109.5(2)
O(1)−Ge(1)−C(11)	112.21(16)	O(1)−Ge(1)−C(11)	108.6(2)
O(2)−Ge(2)−C(19)	107.85(14)	O(2)−Ge(2)−C(19)	111.3(2)
O(2)−Ge(2)−C(15)	105.32(15)	O(2)−Ge(2)−C(15)	106.8(2)
O(3)−Ge(2)−C(19)	107.61(15)	O(3)−Ge(2)−C(19)	107.0(2)
O(3)−Ge(2)−C(15)	109.68(17)	O(3)−Ge(2)−C(15)	111.0(2)
Ge(2)−O(2)−Ge(1)	133.46(15)	Ge(2)−O(2)−Ge(1)	134.4(2)

Table 3. Intermolecular Bond Distances and Angles for Compounds 2a and 2b

atoms	distances (Å)			angles (deg)	
D−H···A	D−H	H···A	D···A	D−H−A	symmetry
2a, O1C−H···O3A	0.497	2.41	2.797	138	−*x*, −*y*, −*z*
2b, O3G−H···O1A	0.850	2.07	2.888	161.5	*x*, −*y*, *z* − $^1/_2$

Results and Discussion

1,3-Di-*tert*-butyl-1,3-diferrocenyldigermoxanediol (2). Ferrocenyl(*tert*-butyl)dichlorogermane (**1a**) was prepared in good yield (80%) by treatment of the [1]-*tert*-butylchlorogermyleneferrocenophane with HCl, eq 1.[11]

$$[(\eta^5\text{-}C_5H_4)_2Fe]Ge(t\text{-}Bu)Cl + HCl \rightarrow FcGe(t\text{-}Bu)Cl_2\ (\mathbf{1a}) \quad (1)$$

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 3a and 3b

3a		3b	
bond length (Å)			
Ge(1)−O(1)	1.773(5)	Ge(1)−O(1)	1.779(4)
Ge(1)−O(3)	1.773(5)	Ge(1)−O(3)	1.768(4)
Ge(2)−O(2)	1.766(5)	Ge(2)−O(2)	1.780(4)
Ge(2)−O(1)	1.766(5)	Ge(2)−O(1)	1.782(3)
Ge(3)−O(3)	1.774(3)	Ge(3)−O(3)	1.763(4)
Ge(3)−O(2)	1.774(5)	Ge(3)−O(2)	1.783(4)
Ge(1)−C(1)	1.914(8)	Ge(1)−C(1)	1.902(6)
Ge(1)−C(11)	1.916(8)	Ge(1)−C(11)	1.928(5)
Ge(2)−C(17)	1.893(8)	Ge(2)−C(17)	1.910(6)
Ge(2)−C(27)	1.926(7)	Ge(2)−C(27)	1.931(6)
Ge(3)−C(33)	1.908(8)	Ge(3)−C(33)	1.917(6)
Ge(3)−C(43)	1.938(8)	Ge(3)−C(43)	1.934(5)
bond angles (deg)			
O(3)−Ge(1)−O(1)	106.2(2)	O(3)−Ge(1)−O(1)	106.98(17)
O(2)−Ge(2)−O(1)	108.1(2)	O(2)−Ge(2)−O(1)	104.09(16)
O(3)−Ge(3)−O(2)	109.2(2)	O(3)−Ge(3)−O(2)	106.54(17)
Ge(2)−O(1)−Ge(1)	125.1(3)	Ge(2)−O(1)−Ge(1)	125.5(2)
Ge(2)−O(2)−Ge(3)	130.2(3)	Ge(2)−O(2)−Ge(3)	121.6(2)
Ge(3)−O(3)−Ge(1)	127.3(3)	Ge(3)−O(3)−Ge(1)	122.6(2)
O(1)−Ge(1)−C(1)	106.4(3)	O(1)−Ge(1)−C(1)	111.6(2)
O(1)−Ge(1)−C(11)	116.2(4)	O(1)−Ge(1)−C(11)	
O(3)−Ge(1)−C(1)	109.1(3)	O(3)−Ge(1)−C(1)	109.0(2)
O(3)−Ge(1)−C(11)	109.7(3)	O(3)−Ge(1)−C(11)	106.7(2)
O(1)−Ge(2)−C(17)	109.2(3)	O(1)−Ge(2)−C(17)	112.6(2)
O(1)−Ge(2)−C(27)	111.1(3)	O(1)−Ge(2)−C(27)	108.6(2)
O(2)−Ge(2)−C(17)	118.0(3)	O(2)−Ge(2)−C(17)	109.6(2)
O(2)−Ge(2)−C(27)	107.4(3)	O(2)−Ge(2)−C(27)	111.3(2)
O(2)−Ge(3)−C(33)	108.9(3)	O(2)−Ge(3)−C(33)	108.9(2)
O(2)−Ge(3)−C(43)	104.6(3)	O(2)−Ge(3)−C(43)	107.5(2)
O(3)−Ge(3)−C(33)	105.9(3)	O(3)−Ge(3)−C(33)	109.7(2)
O(3)−Ge(3)−C(43)	108.1(3)	O(3)−Ge(3)−C(43)	108.9(2)
C(1)−Ge(1)−C(11)	116.2(4)	C(1)−Ge(1)−C(11)	114.0(2)
C(17)−Ge(2)−C(27)	112.8(3)	C(17)−Ge(2)−C(27)	110.5(2)
C(33)−Ge(3)−C(43)	119.9(3)	C(33)−Ge(3)−C(43)	114.9(2)

The ^1H and ^{13}C spectra of **1a** are completely consistent with the proposed structure and related literature data for ferrocenyl-substituted chlorogermanes.[11] Hydrolysis of **1a** was performed according to the published proce-

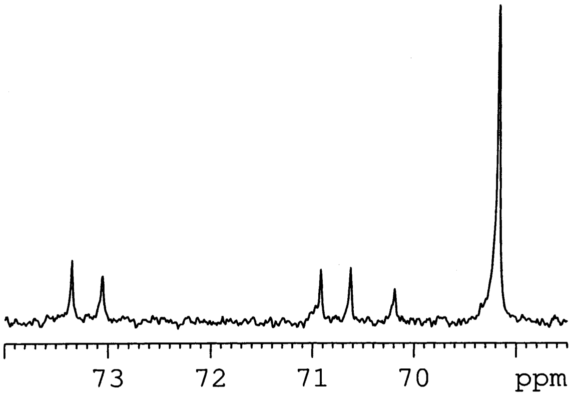


Figure 1. ^{13}C NMR spectrum (η^5-C_5H_5 region in C_6D_6) of 1,3-di-*tert*-butyl-1,3-diferrocenyldigermoxanediol (**2**) showing that all the carbon atoms on the substituted Cp ring are chemically inequivalent.

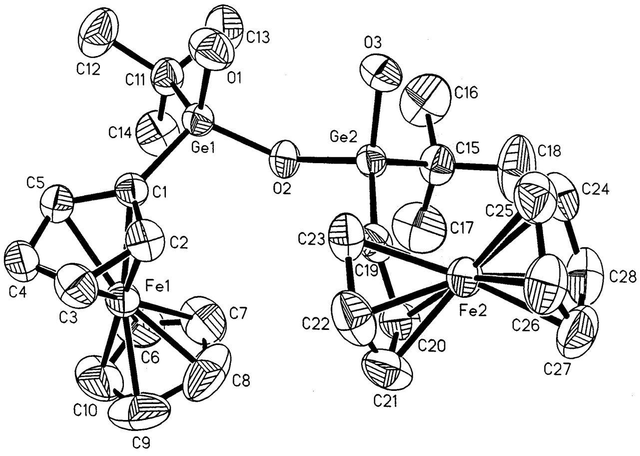


Figure 2. Molecular structure of 1,3-di-*tert*-butyl-1,3-diferrocenyldigermoxanediol (**2a**).

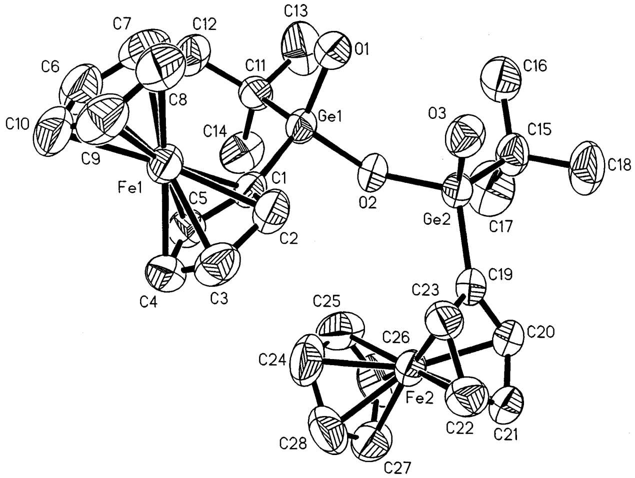
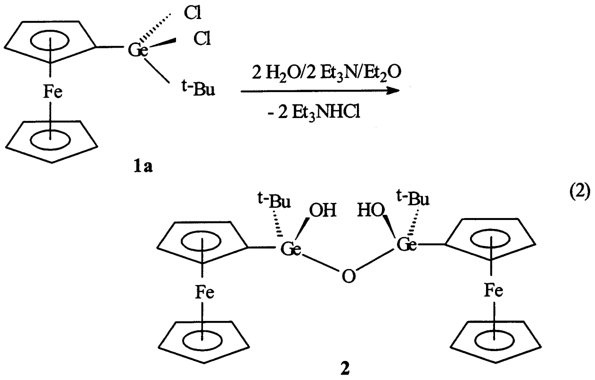


Figure 3. Molecular structure of 1,3-di-*tert*-butyl-1,3-diferrocenyldigermoxanediol (**2b**).

dure for the preparation of organosilanols with slight modifications, eq 2.[6]



1a

2

(2)

Unlike its silicon analogues,[6] the hydrolysis of **1a** did not form the expected germanediols but gave directly the ferrocenyl-substituted digermoxanediol, **2**. This is the first example of a ferrocenyl-containing digermoxanediol. It is interesting that **2** was formed only as the meso isomer. The ^{13}C NMR spectrum exhibits six different cyclopentadienyl resonances (Figure 1), one for the free C_5H_5 ring and five for the nonequivalent C atoms of the C_5H_4 group. However, the ^1H NMR spectrum exhibits a broad singlet for 16 of the protons of this material with a small resonance for the other 2, as noted for the Si diferrocenyl analogue.[7] A typical broad resonance at 2.41 ppm is noted for the exchanging OH protons in C_6D_6; in $CDCl_3$ an upfield shift resonance is observed, ~0.56 ppm for these protons.

For hydroxyl-containing compounds, the growth of single crystals greatly depends on the polarity of the solvents utilized. Thus, two different types of single crystals of **2** were obtained from different solvents, **2a** (benzene) and **2b** (a mixture of THF and benzene). The molecular structures of **2a** and **2b** are illustrated in Figures 2 and 3, respectively. Tables 2 and 3 provide selected bond lengths and angles and intermolecular bond distances and angles, respectively.

The X-ray crystal structure of **2a** shows that it belongs to the triclinic space group $P\bar{1}$ with $Z = 2$. The unit cell exhibits an independent pair of hydrogen-bonded centrosymmetric dimeric units, Figure 4. The Ge−O bond lengths range from 1.781 to 1.786 Å for the Ge−OH groups and from 1.768 to 1.774 Å for the Ge−O−Ge function. These values are almost identical with those in $(t\text{-}Bu_2GeOH)_2O$.[12] The Ge−O−Ge angle of 133.45(17)° is close to the corresponding values reported for $(Ph_3Ge)_2O$ (135.2°)[13] and $[CpFe(CO)_2GeMe_2]_2O$ (134°),[14] but much smaller than that in $(t\text{-}Bu_2GeOH)_2O$ (143.9°).[12] From Figure 4 one can observe that in each germoxane moiety the two Fc groups are arranged in a typical orthogonal arrangement with an Fe···Fe intramolecular distance of 6.56 Å. This arrangement is remarkably similar to that observed in the structure of $(FcMe_2Si)_2O$ (**4**) and such Fc···Fc interactions can contribute to the overall stabilization of the solid-state structure.[2i] A view down the Ge−O−Ge linkage, Figure 5, indicates that, as with **4**, there is a semieclipsed structure, presumably to facilitate the Fc···Fc interaction.

The X-ray crystal structure of **2b** shows that it belongs to the monoclinic space group *C*2/*c* with $Z = 8$. In this structural form the digermoxanediol exhibits an organometallic supramolecular array[15] consisting of a hydrogen-bonded double-chain structure (Figure 6) in which all hydrogen bonds are intermolecular. With

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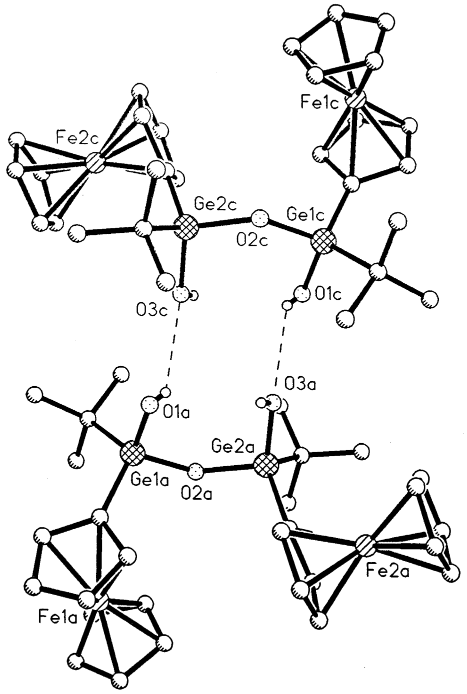


Figure 4. Stereodiagram of **2a** as a hydrogen-related dimeric unit.

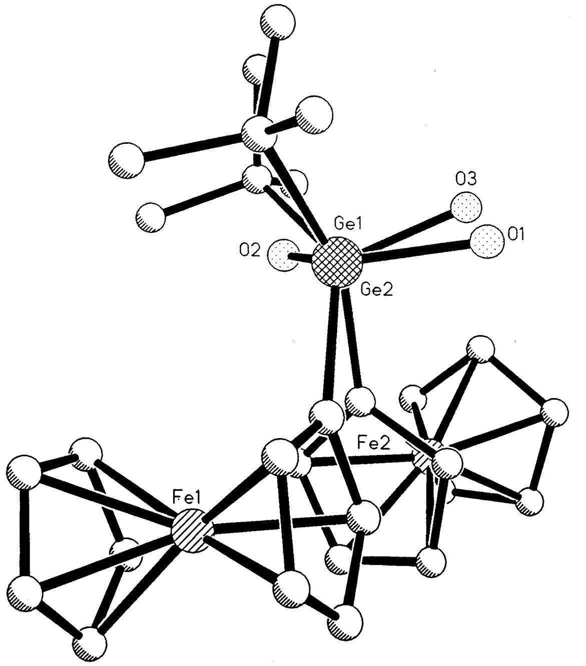


Figure 5. A projection about Ge−O−Ge for **2a**.

respect to the two chains, one results from the *c*-glide plane in the space group *C*2/*c* and the translational symmetry along the *z*-axis acting on the molecule, which is in this case the asymmetric unit of the structure. The other one also results from the *c*-glide and the *z*-translation but acting on the inverted molecule. This produces the two chains running in opposite directions and related by a center of symmetry.

Within each digermoxane unit the intramolecular Fc···Fc orientation is again orthogonal, with an Fe···Fe separation of 6.47 Å. The average Ge−O bond lengths of 1.766 Å for Ge−OH and 1.785 Å for Ge−O−Ge, and the Ge−O−Ge angles of 134.4(2)°, are essentially equivalent with those related data in **2a**.

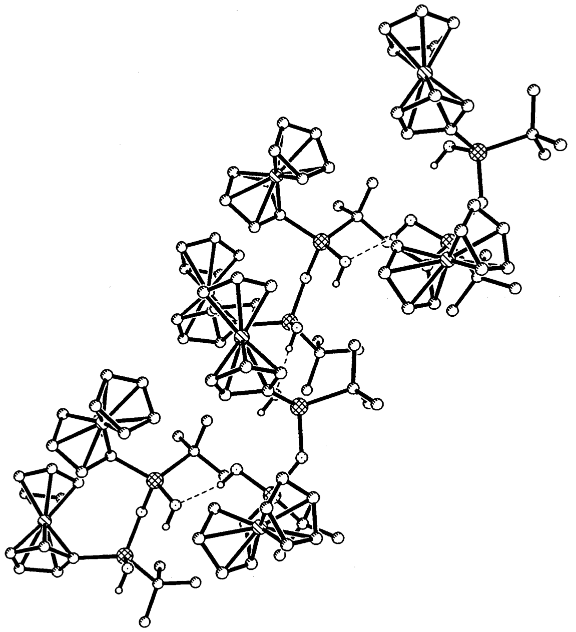
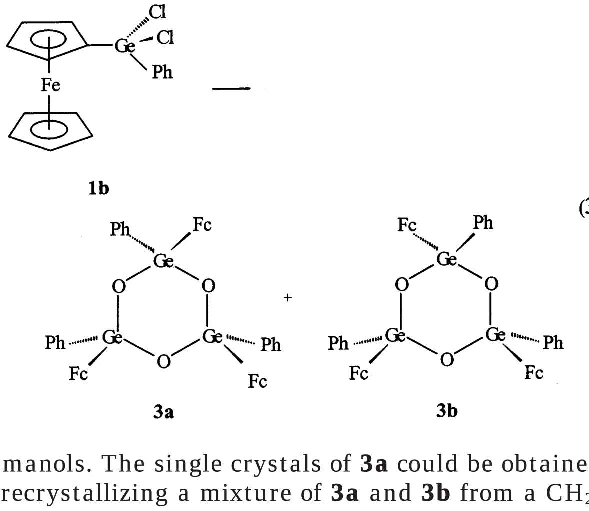


Figure 6. Stereodiagram of **2b** showing the hydrogen-bonded chains.

Indeed the individual germoxane molecular structures of **2a** and **2b** are almost identical. The sole distinction is a clear decrease in one O−Ge−OH bond angle in **2a** to **2b**, 107° to 102°, with concomitant increase in the C_{Fc}−Ge−OH angle from 104° to 109°, to better incorporate the dimeric nature of **2a**. Despite this minor change the longer intermolecular H···O bond distances and smaller O−H···O angle in **2a** than those in **2b** (2.41 Å vs 2.07 Å, 138° vs 161.5°) demonstrate that there is weaker hydrogen bonding in **2a**.

***cis*- and *trans*-1,3,5-Triphenyl-1,3,5-triferrocenylcyclotrigermoxane (3a and 3b).** Hydrolysis of ferrocenyl(phenyl)dichlorogermane (**1b**) produced a mixture of *cis*-cyclotrigermoxane (**3a**) and *trans*-cyclotrigermoxane (**3b**), with the latter predominant (**3a**:**3b** = 1:4), eq 3. We obtained no evidence for the intermediacy of



(3)

germanols. The single crystals of **3a** could be obtained by recrystallizing a mixture of **3a** and **3b** from a CH_2Cl_2/hexane solution; however, we were unable to obtain the pure trans isomer **3b** by recrystallization or column chromatography. However, thermal treatment of a mixture of **3a** and **3b** in 95% ethanol solution, in the presence of a catalytic amount of NaOH, afforded the pure trans isomer **3b**. A solution of pure **3a** in C_6D_6

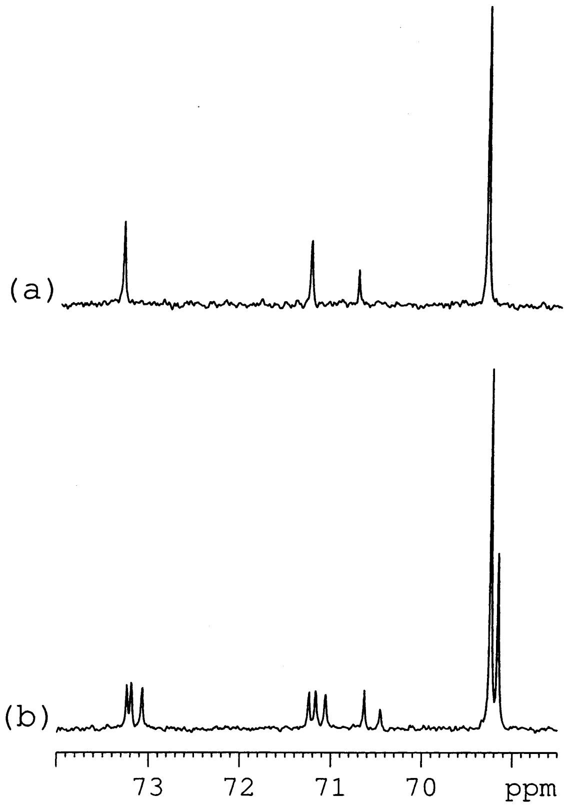


Figure 7. (a) ^{13}C NMR spectrum (η^5-C_5H_5 region in C_6D_6) of *cis*-1,3,5-triphenyl-1,3,5-triferrocenylcyclotrigermoxane (**3a**). (b) ^{13}C NMR spectrum (η^5-C_5H_5 region in C_6D_6) of *trans*-1,3,5-triphenyl-1,3,5-triferrocenylcyclotrigermoxane (**3b**).

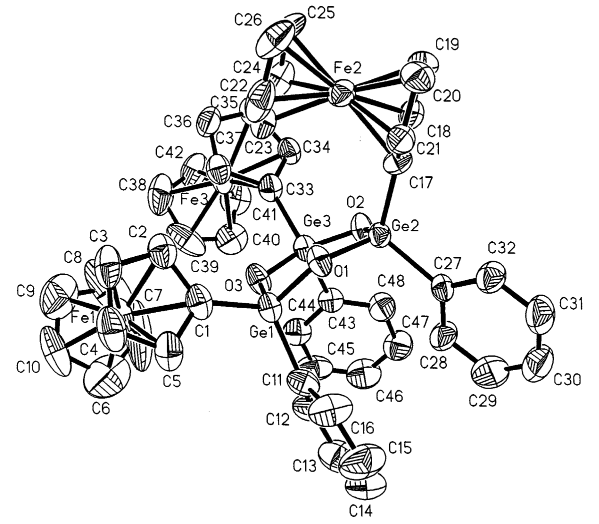


Figure 8. Molecular structure of *cis*-1,3,5-triphenyl-1,3,5-triferrocenylcyclotrigermoxane (**3a**).

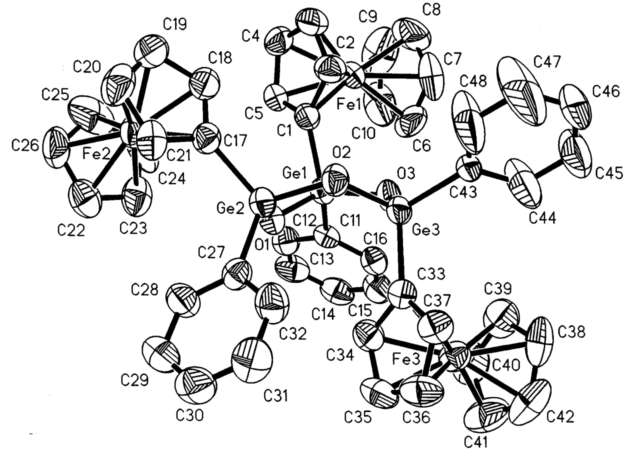


Figure 9. Molecular structure of *trans*-1,3,5-triphenyl-1,3,5-triferrocenylcyclotrigermoxane (**3b**).

stored at room temperature for two months transformed to a mixture of both **3a** and **3b** as a ratio of 3:1 as noted by NMR spectroscopy. This process is much less facile than that for the related stannasiloxanes.[6]

The ^{1}H and ^{13}C NMR spectra of **3a** and **3b** are in total accord with the proposed structures. The ^{13}C NMR spectrum of the cis isomer **3a** exhibits the expected four resonances for the ferrocenyl groups and four resonances for the phenyl groups, indicating that the cis-adjacent Fc and phenyl groups are equivalent (Figure 7). The ^{13}C NMR spectrum of the trans isomer **3b** shows two sets of resonances in both the Cp and phenyl regions in the approximately 2:1 ratio expected.

The molecular structures of **3a** and **3b** are illustrated in Figures 8 and 9, respectively. Table 4 provides selected bond lengths and angles. Both **3a** and **3b** can formally be considered as derived from *cyclo*-($Ph_2GeO)_3$.[16]

The X-ray crystal structure of **3a** shows that it belongs to the monoclinic space group $P2_1/n$ with $Z = 4$. In the molecule, both the ferrocenyl and phenyl groups adopt cis configuration. The adjacent intramolecular Fc···Fc separation ranges from 6.64 to 7.37 Å. The values for the average Ge−O bond lengths (1.771 Å) and for the average Ge−O−Ge angles (127.5°) are in the normal range thus far noted for such cyclic organogermoxanes and compare to values of 1.77 Å and 129° for *cyclo*-($Ph_2GeO)_3$, 1.781 Å and 133.0° for *cyclo*-(*t*-$Bu_2GeO)_3$,[17] 1.765 Å and 127.1° for *cyclo*-*t*-$Bu_2Sn(OGePh_2)_2O$,[18] and 1.795 Å and 126.1° for *cyclo*-($Me_4Ge_2O)_2$.[19]

The X-ray crystal structure of **3b** shows that it belongs to the triclinic space group $P\bar{1}$ with $Z = 2$ and the molecule exhibits a trans, 2-up, 1-down, configuration. The trans Fc group is almost parallel to one of the two cis Fc groups but is orthogonal to the other one. As expected, the adjacent cis Fe···Fe separation (6.57 Å) is smaller than the separations (8.05 and 8.96 Å) between the trans oriented Fc groups. The average Ge−O bond length of 1.776 Å is very close to those in the isomeric **3b**, but the average Ge−O−Ge angle of 123.2° is less than those in **3b**.

Acknowledgment. This research was supported by the Robert. A. Welch Foundation, Houston, TX.

Supporting Information Available: Listings of crystal data, data collection, solution and refinement, complete atomic coordinates, bond distances and angles, and anisotropic thermal parameters for **2a**, **2b**, **3a**, and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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