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Ring-Opening Polymerization of Strained, Ring-Tilted [1]Ferrocenophanes with Germanium in the Bridge: Structures of the [1]Germaferrocenophane $Fe(\eta\text{-}C_5H_4)_2GeMe_2$ and the Ferrocenylgermane $Fe(\eta\text{-}C_5H_4GeEt_2Cl)(\eta\text{-}C_5H_5)$

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The germanium-bridged [1]ferrocenophanes $Fe(\eta\text{-}C_5H_4)_2GeR_2$ (**3a**−**c**: **a**, R = Me, **b**, R = Et, and **c**, R = Ph) have been prepared via the reaction of $Fe(\eta\text{-}C_5H_4Li)_2\cdot$TMEDA (TMEDA = tetramethylethylenediamine) with the appropriate dichloroorganogermane R_2GeCl_2. The monosubstituted ferrocenylgermane $Fe(\eta\text{-}C_5H_4GeEt_2Cl)(\eta\text{-}C_5H_5)$ (**5**) was isolated as a byproduct from the synthesis of **3b**. An X-ray diffraction study of **3a** revealed that this molecule possesses a highly strained, ring-tilted structure with an angle between the planes of the cyclopentadienyl rings of 19.0(9)°. The Fe−Ge distance (2.804(2) Å) in **3a** is ca. 18% longer than the sum of the covalent radii (2.38 Å) and is consistent with a weak dative interaction. This conclusion was also supported by ^{57}Fe Mössbauer spectroscopic data for this species. The monosubstituted ferrocenylgermane **5** was also studied by single crystal X-ray diffraction. In this species the two cyclopentadienyl rings are modestly inclined toward each other in an opposite sense to those in **3a** by 4.5(9)°. However, interestingly, the $GeEt_2Cl$ fragment is tilted significantly toward the iron center with an angle between the plane of the cyclopentadienyl ligand to which it is attached and the C(ipso)−Ge bond of 7.5(7)°. The Fe−Ge distance (3.412(5) Å), although ca. 42% longer than the sum of the covalent radii, is consistent with a very weak dative interaction similar to that in ferrocene-stabilized carbocations such as $[Fe(\eta\text{-}C_5H_4CPh_2)(\eta\text{-}C_5H_5)]^+$ (**6**). Compounds **3a**−**c** were found to undergo facile ring-opening polymerization when heated in the melt to yield high molecular weight ($M_w = (1.0 \times 10^6)-(2.0 \times 10^6)$ and $M_n = (2.3 \times 10^5)-(8.5 \times 10^5)$) poly(ferrocenylgermanes) $[Fe(\eta\text{-}C_5H_4)_2GeR_2]_n$ **7a**−**c**. Compounds **3a** and **3b** were found to be sensitive to moisture and afforded the ferrocenylgermoxanes **8a** and **8b** when exposed to the atmosphere. Crystals of **3a** are triclinic, space group $P\bar{1}$, with $a = 7.269(3)$ Å, $b = 8.426(4)$ Å, $c = 9.273(4)$ Å, $\alpha = 82.96(4)°$, $\beta = 78.78(4)°$, $\gamma = 80.07(3)°$, $V = 546.4(3)$ Å^3, and $Z = 2$. Crystals of **5** are tetragonal, space group $I4_1/a$, with $a = 12.307(4)$ Å, $c = 38.690(10)$ Å, $V = 5860(2)$ Å^3, and $Z = 16$.

Introduction

Polymers containing skeletal transition metal atoms are of considerable interest because of their unusual physical and chemical properties.[1,2] However, until recently, relatively few well-characterized, high molecular weight, and soluble examples of these materials had been reported.[2] As part of our program to explore the use of ring-opening polymerization (ROP) as route to macromolecules containing transition metals in the main chain, we reported the discovery that strained, ring-tilted [1]ferrocenophanes **1a** and **1b** containing silicon in the bridge undergo thermal ROP to yield high molecular weight poly(ferrocenylsilanes).[3] This ROP route has subsequently been found to be very general and provides a route to a structurally diverse series of well-defined, high molecular weight, and, in virtually all cases, soluble poly(ferrocenylsilanes) **2**, which display a range of interesting properties.[4−6] The driving force for these facile ROP reactions is derived from the ring-strain present in the [1]silaferrocenophane monomers which has been measured to be ca. 80 kJ mol^{-1} for **1a**.[3]

The discovery of the ROP of **1a** and **1b** suggested that related metallocenophanes might also function as precursors to novel polymers.[3] We have subsequently

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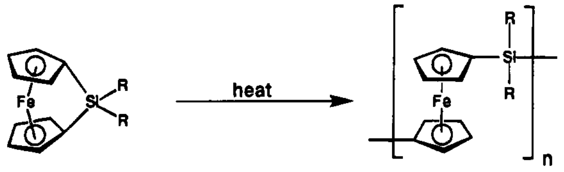
found that related [1]ferrocenophanes containing other elements in the bridge and [2]metallocenophanes with a hydrocarbon bridge also polymerize thermally.[7-9] In this paper, as a follow-up to our communication,[8a] we give full details of our work on the synthesis, structure, and ROP of a series of germanium-bridged [1]ferrocenophanes.



1

a R = Me
b R = Ph

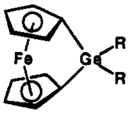
2

a R = Me
b R = Ph

Results and Discussion

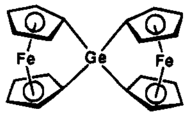
Synthesis of the [1]Germaferrocenophanes 3a–c and the Isolation of the Ferrocenylgermane 5. The first reported [1]ferrocenophane containing a single germanium atom in the bridge was $Fe(\eta\text{-}C_5H_4)_2GePh_2$ (**3c**) prepared by Osborne and co-workers in 1980 from the reaction of $Fe(\eta\text{-}C_5H_4Li)_2{\cdot}TMEDA$ (TMEDA = tetramethylethylenediamine) with Ph_2GeCl_2 in hexanes.[10] An X-ray crystal diffraction study of **3c** revealed that the tilt-angle α between the planes of the cyclopentadienyl ligands in this species was 16.6(15)°. This value is indistinguishable from that found for the analogous silicon-bridged compound **1b** (α = 19.2(10)°) due to the relatively low accuracy of the structure determinations.[11,12] The only other reported germanium-bridged [1]ferrocenophane was the spirocyclic species $[Fe(\eta\text{-}C_5H_4)_2]_2Ge$, **4**, which was also prepared by Osborne et al.[13] This compound, which was characterized spectroscopically and by elemental analysis, was isolated in low yield from the reaction of two equivalents of $Fe(\eta\text{-}C_5H_4Li)_2{\cdot}TMEDA$ with $GeCl_4$.[13]

The new germanium-bridged [1]ferrocenophanes **3a** and **3b**, together with **3c**, were synthesized by the salt elimination reactions of $Fe(\eta\text{-}C_5H_4Li)_2{\cdot}TMEDA$ with the appropriate dihaloorganogermane.[14] The monomers **3a–c** were isolated as orange-red, moisture-sensitive, crystalline materials in relatively low yield (ca. 30–35%) after purification by vacuum sublimation. The [1]germaferrocenophanes **3a** and **3b** were characterized by ^1H and ^{13}C NMR and mass spectrometry, while the identity of **3c** was confirmed by ^1H NMR spectroscopy which afforded a spectrum consistent with that previously reported.[10] The ^1H and ^{13}C NMR spectra of **3a** and **3b** were consistent with the assigned structures and their mass spectra showed the presence of intense peaks corresponding to the molecular ions. The ^{13}C NMR chemical shifts for the resonances assigned to the ipso carbon atoms for **3a** and **3b** were 30.1 and 30.0 ppm, respectively, and show a dramatic high-field shift compared to those for analogous unbridged species. This feature is characteristic of strained [1]ferrocenophanes with main group elements in the bridge.[10] The ^1H NMR spectra of **3a** and **3b** showed two pseudo triplets in the cyclopentadienyl region (4.0–4.5 ppm) characteristic of an A_2B_2 spin system. The large separation between the pseudo triplets of 0.3–0.4 ppm for **3a** and **3b** is also typical for [1]ferrocenophanes containing a main group element in the bridge. This is large in comparison to analogous unbridged ferrocenes where the separation is less than 0.2 ppm and is also indicative of substantial strain in these molecules.[10] The unbridged ferrocenylgermane $Fe(\eta\text{-}C_5H_4GeEt_2Cl)(\eta\text{-}C_5H_5)$, **5**, was isolated in low yield (ca. 10%) as a side product from the preparation of **3b**. This species is presumably derived from the reaction of Et_2GeCl_2 with small quantities of monolithioferrocene present in the sample of dilithioferrocene used for the reaction. Compound **5** was also successfully synthesized in good yield (65%) from the reaction of Et_2GeCl_2 with monolithioferrocene, which was prepared from chloromercuriferrocene[15] and *n*-BuLi. Compound **5** was identified by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and a single crystal X-ray diffraction study (see below). The ^1H and ^{13}C NMR spectra showed the presence of both a substituted and an unsubstituted cyclopentadienyl ring along with resonances assigned to the ethyl groups attached to germanium. In addition, the mass spectrum of **5** showed the presence of the molecular ion as the base peak.



3

a R = Me
b R = Et
c R = Ph



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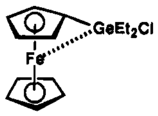

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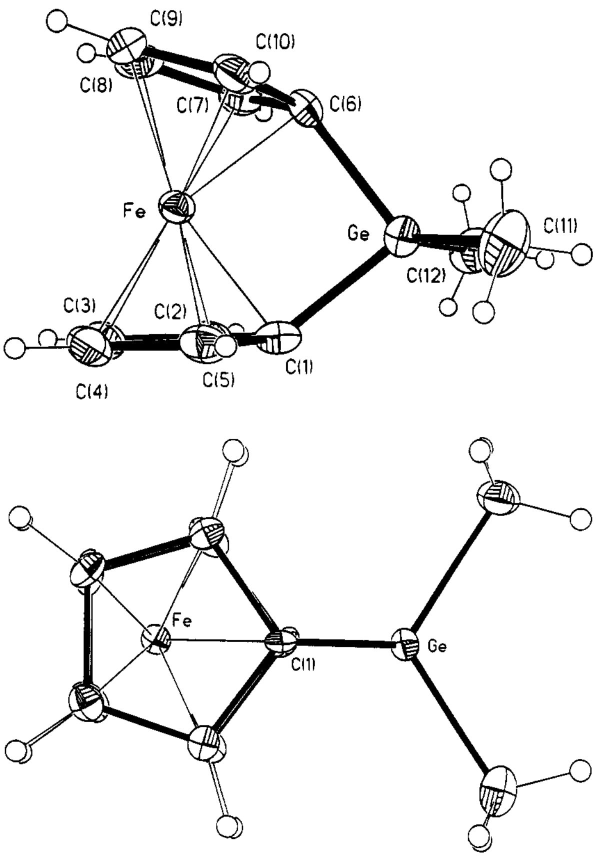

Figure 1. (a, top) Molecular structure of **3a** (with thermal ellipsoids drawn at the 25% probability level). (b, bottom) Alternative view of a molecule of **3a** (with thermal ellipsoids drawn at the 25% probability level).

X-ray Structure of the [1]Germaferrocenophane 3a. As only one [1]ferrocenophane with a germanium atom in the bridge (**3c**) had been previously crystallographically characterized and in order to allow a detailed comparison with related species, **3a** was studied by single-crystal X-ray diffraction. Orange-red crystals of **3a** suitable for an X-ray study were obtained via vacuum sublimation. Figure 1 shows two alternative views of the molecular structure of **3a**. A summary of cell constants and data collection parameters is included in Table 1, and the fractional coordinates and selected bond lengths and angles are listed in Tables 2 and 3. A summary of important structural features for **3a** and related species is presented in Table 6.

The structural features of **3a** can be compared to those of both the diphenyl analogue **3c** and the silicon analogue **1a**.[4b,11] As was found for both of the latter species, the cyclopentadienyl rings of **3a** are virtually eclipsed and are each essentially planar; a mean deviation of 0.003 Å from the weighted least squares plane containing C(1)–C(5) and 0.008 Å for the C(6)–C(10) plane is present. The tilting of the planes of the cyclopentadienyl ligands with respect to one another in **3a** (α = 19.0(9)°) is similar to that detected in **3c** (α = 16.6(15)°) although the large estimated standard deviation for **3c** makes a meaningful comparison difficult. Similar comments apply to the Ge–C_{ipso} bond lengths in **3a** and **3c** which are similar (**3a**, 1.978(6) Å, vs **3c**, 1.960(10) Å). The tilt-angle between the planes of the cyclopentadienyl ligands in **3a** (α = 19.0(9)°) is slightly less than that in **1a** (α = 20.8(5)°). This is consistent with the slightly larger covalent radius of germanium (1.22 Å) compared to that of silicon (1.17 Å).[16] The values of the angle, β, between the planes of the cyclopentadienyl ligands and the C(ipso) bridging atom bonds for **3a**, **3c**, and **1a** indicate similarly large distortions from planarity at the ipso carbon atom (β = 37.7(5)° and 35.9(5)° for **3a**, β = 38.2(8)° for **3c**, β = 37.0(6)° for **1a**). The C_{ipso}–Ge–C_{ipso} bond angle in **3a** (91.7(3)°) is significantly smaller than the ideal tetrahedral value (109.5°). Consequently, a scissoring effect is observed, giving rise to a wider bond angle between the methyl substituents and the Ge center (113.5(3)°).[17] A similar effect is observed in both **3c** and **1a**. It is noteworthy that the Cp_{ipso}–X–Cp_{ipso} bond angles at germanium for **3a** (91.7(3)°) and **3c** (93.6(4)°) are significantly smaller than that found at silicon for **1a**

Table 1. Summary of Crystal Data and Intensity Collection Parameters

	3a	5
empirical formula	$C_{12}H_{14}FeGe$	$C_{14}H_{19}ClFeGe$
M_r	286.7	351.2
cryst class	triclinic	tetragonal
space group	$P\bar{1}$	$I4_1/a$
a, Å	7.269(3)	12.307(4)
b, Å	8.426(4)	
c, Å	9.273(4)	38.690(10)
α, deg	82.96(4)	
β, deg	78.78(4)	
γ, deg	80.07(3)	
V, Å^3	546.4(3)	5860(2)
Z	2	16
D_{calc}, g cm^{-3}	1.742	1.592
μ(Mo Kα), cm^{-1}	0.40	0.32
F(000)	288	2848
ω-scan width, deg	0.60 + 0.35 tan θ	0.75 + 0.35 tan θ
range θ collected, deg	2.0 to 22.5	1.0 to 22.5
total no. of rflns	1345	1832
no. of unique rflns	1345	1666
R_{int}	0.000	0.063
no. of obsd data used [$I > 3\sigma(I)$]	1177	1234
weighting g	0.0018	0.0029
R	0.040	0.051
R_w	0.060	0.072
GOF	1.31	1.09
$(\Delta/\sigma)_{max}$ in last cycle	0.019	0.007
no. of params refined	129	155
$\Delta\varrho$ (max) in final ΔF map, e Å^{-3}	0.68	0.58

Table 2. Final Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å × 10^3) for the Non-Hydrogen Atoms of 3a

	x	y	z	U(eq)[a]
Ge	2474(1)	1614(1)	1462(1)	23(1)
Fe	4329(1)	2981(1)	3275(1)	20(1)
C(1)	5158(8)	1467(7)	1663(7)	24(2)
C(2)	5742(8)	713(7)	3018(7)	25(2)
C(3)	6939(9)	1671(7)	3432(7)	30(2)
C(4)	7144(9)	3013(8)	2361(7)	30(2)
C(5)	6044(8)	2881(7)	1280(7)	27(2)
C(6)	1624(8)	3102(7)	3035(7)	23(2)
C(7)	1842(8)	2521(7)	4523(6)	26(2)
C(8)	2490(9)	3714(8)	5159(7)	33(2)
C(9)	2709(8)	5042(7)	4117(7)	29(2)
C(10)	2147(8)	4686(7)	2819(7)	28(2)
C(11)	1997(11)	2669(9)	−433(7)	45(3)
C(12)	1547(10)	−439(8)	1962(8)	41(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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Table 3. Selected Distances (Å) and Angles (deg) for 3a (Esd's Are in Parentheses)

Distances			
Fe–Ge	2.804(2)	Ge–C(11)	1.936(7)
Fe–C(1)	2.019(6)	Ge–C(12)	1.935(7)
Fe–C(2)	2.026(6)	C(1)–C(2)	1.443(8)
Fe–C(3)	2.046(6)	C(1)–C(5)	1.426(9)
Fe–C(4)	2.060(6)	C(2)–C(3)	1.416(10)
Fe–C(5)	2.022(6)	C(3)–C(4)	1.419(9)
Fe–C(6)	2.006(6)	C(4)–C(5)	1.424(10)
Fe–C(7)	2.019(6)	C(6)–C(7)	1.436(8)
Fe–C(8)	2.072(6)	C(6)–C(10)	1.430(9)
Fe–C(9)	2.069(6)	C(7)–C(8)	1.413(10)
Fe–C(10)	2.021(6)	C(8)–C(9)	1.396(9)
Ge–C(1)	1.977(6)	C(9)–C(10)	1.424(10)
Ge–C(6)	1.978(6)		
Angles			
C(1)–Ge–C(6)	91.7(3)	C(11)–Ge–C(12)	113.5(3)
C(1)–Ge–C(11)	112.1(3)	Ge–C(1)–C(2)	118.9(4)
C(1)–Ge–C(12)	112.7(3)	Ge–C(1)–C(5)	118.6(4)
C(6)–Ge–C(11)	111.5(3)	Ge–C(6)–C(7)	119.3(4)
C(6)–Ge–C(12)	113.4(3)	Ge–C(6)–C(10)	120.3(4)

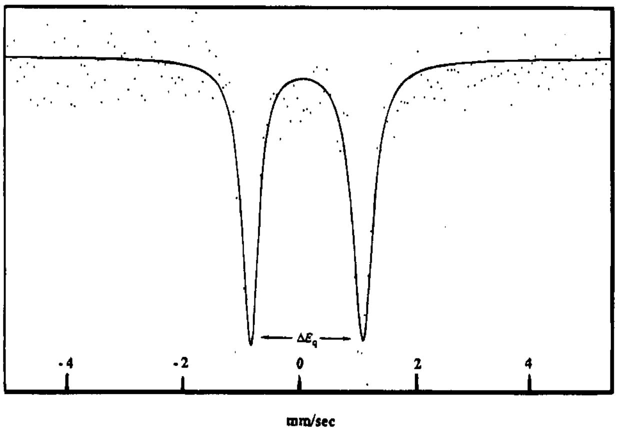

Figure 2. Room temperature ^{57}Fe Mössbauer spectrum of **3a**.

(95.7(4)°). The Fe–Ge distance in **3a** (2.804(2) Å) is longer than that in **3c** (2.744(3) Å). The Fe–Ge distances in both of these structures lie outside the range of the sum of the covalent radii (2.38 Å) and are in fact ca. 18% and ca. 15% longer than those calculated for a Fe–Ge single bond in **3a** and **3c**, respectively.[16] As previously noted by Silver, bond lengths of 2.377(2) Å[18] and 2.430(2) Å[19] have been established for Fe–Ge bonds; thus interactions probably exist in both **3a** and **3c** with a bond order less than 1.[20] The extent of the iron–bridging atom interaction for **3a** and **3c** can be compared to the Si analogues where the Fe–Si distances of 2.690(3) Å for **1a** and 2.636(5) Å for **1b** are ca. 15% and ca. 13% longer than the sum of the covalent radii (2.33 Å), respectively. As in the case of **3c**, the bonding interaction in **3a** is believed to involve the filled 3d orbitals ($3d_{xy}$ and $3d_{x^2-y^2}$) of the Fe atom which possess e_2 symmetry and the symmetry related empty 4d orbitals of the Ge atom.[20]

The Mössbauer Spectrum of 3a. The room-temperature Mössbauer spectrum of **3a** (Figure 2) was obtained in order to allow a comparison with data previously obtained by Osborne for the compound **3c**.[10]

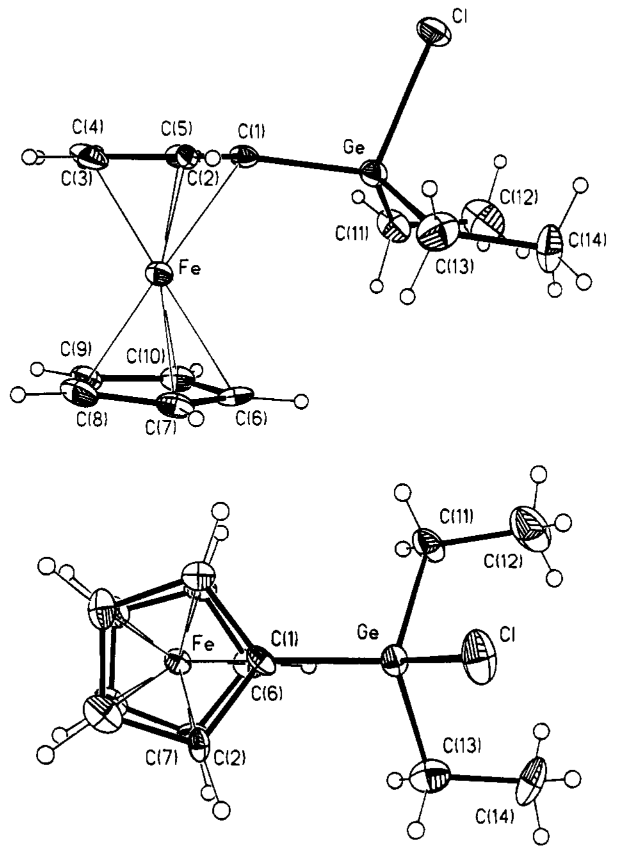

Figure 3. (a, top) Molecular structure of **5** (with thermal ellipsoids drawn at the 25% probability level). (b, bottom) Alternative view of a molecule of **5** (with thermal ellipsoids drawn at the 25% probability level).

This isomer shift value δ (relative to Fe foil) for **3a** was 0.333(5) mm s^{-1}, while the quadrupolar splitting value ΔE_q was 2.102(5) mm s^{-1}. The corresponding values for **3c** were $\delta = 0.43$ mm s^{-1} and $\Delta E_q = 2.01$ mm s^{-1}.[10] The quadrupolar splitting values for **3a** and **3c** are both smaller than that of ferrocene (2.42 mm s^{-1}) and provide evidence for the presence of a weak dative Fe–Ge bond.[20] The differences in the quadrupolar splitting values between **3a** and **3c** can probably be attributed to the relative Fe–Ge dative bond strengths which are reflected by the Fe–Ge distances in each compound (2.804(2) Å in **3a** vs 2.744(3) Å in **3c**). The longer and hence weaker dative bond in **3a** compared to **3c** is presumably a consequence of the more electron deficient germanium center in the latter compound.

X-ray Structure of 5. In order to investigate whether an iron–germanium interaction similar to that in **3a** could occur in a nonbridged species and due to the virtual absence of structural data on ferrocenylhalogenosilanes[21] and germanes,[22] compound **5** was studied by single crystal X-ray diffraction. Compound **5** was isolated as a liquid at 25 °C. Golden-yellow crystals for X-ray studies were isolated via recrystallization from hexanes at −30 °C over a 2 week period. Figure 3 shows two alternative views of the molecular structure of **5**. A

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[18] Adams, R. D.; Cotton, F. A.; Frenz, B. A. *J. Organomet. Chem.* **1974**, *73*, 93.

[19] Curtis, M. D.; Butler, W. A.; Scibelli, J. *J. Organomet. Chem.* **1980**, *192*, 209.

[20] Silver, J. *J. Chem. Soc., Dalton Trans.* **1990**, 3513.

[21] Butler, I. R.; Cullen, W. R.; Rettig, S. J. *Can. J. Chem.* **1987**, *65*, 1452.

[22] Several ferrocenylgermane compounds containing a Ge–Cl bond have been prepared. However, to the best of our knowledge, none of these materials have been structurally characterized. See for instance: (a) Seyferth, D.; Hofman, H. P.; Burton, R.; Helling, J. F. *Inorg. Chem.* **1962**, *1*, 227. (b) Sollot, G. P.; Peterson, W. R. *J. Am. Chem. Soc.* **1967**, *89*, 6783.

Table 4. Final Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å $\times$ 10^3) for the Non-Hydrogen Atoms of 5

	x	*y*	*z*	*U*(eq)[a]
Fe	2211(1)	5218(1)	1118(1)	27(1)
Ge	2438(1)	6735(1)	383(1)	32(1)
Cl	2422(3)	8473(2)	235(1)	57(1)
C(11)	1191(10)	6114(10)	148(3)	49(4)
C(12)	1132(14)	6348(12)	−236(4)	83(7)
C(13)	3864(10)	6240(11)	253(4)	58(5)
C(14)	4092(12)	6248(12)	−142(3)	75(6)
C(1)	2255(7)	6690(7)	871(3)	28(3)
C(2)	3107(8)	6598(7)	1128(2)	27(3)
C(3)	2646(9)	6426(8)	1450(3)	45(4)
C(4)	1506(9)	6390(8)	1407(3)	39(4)
C(5)	1268(8)	6560(8)	1057(3)	32(4)
C(6)	2395(8)	3959(7)	775(3)	39(4)
C(7)	3214(8)	3920(7)	1044(3)	34(4)
C(8)	2676(8)	3839(8)	1361(3)	43(4)
C(9)	1555(9)	3816(8)	1300(3)	39(4)
C(10)	1391(8)	3912(8)	943(3)	36(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Selected Distances (Å) and Angles (deg) for 5 (Esd's Are in Parentheses)

Distances			
Fe−Ge	3.412(5)	Ge−Cl	2.214(3)
Fe−C(1)	2.049(9)	C(1)−C(2)	1.449(13)
Fe−C(2)	2.026(9)	C(1)−C(5)	1.422(14)
Fe−C(3)	2.036(11)	C(2)−C(3)	1.386(15)
Fe−C(4)	2.020(10)	C(3)−C(4)	1.41(2)
Fe−C(5)	2.032(10)	C(4)−C(5)	1.398(15)
Fe−C(6)	2.053(11)	C(6)−C(7)	1.45(2)
Fe−C(7)	2.040(10)	C(6)−C(10)	1.399(14)
Fe−C(8)	2.023(11)	C(7)−C(8)	1.40(2)
Fe−C(9)	2.031(10)	C(8)−C(9)	1.400(15)
Fe−C(10)	2.014(10)	C(9)−C(10)	1.40(2)
Ge−C(1)	1.901(10)	C(11)−C(12)	1.51(2)
Ge−C(11)	1.941(12)	C(13)−C(14)	1.56(2)
Ge−C(13)	1.925(12)		
Angles			
C(1)−Ge−C(11)	111.1(4)	C(13)−Ge−Cl	104.3(4)
C(1)−Ge−C(13)	110.9(5)	Ge−C(1)−C(2)	126.7(7)
C(1)−Ge−Cl	106.5(3)	Ge−C(1)−C(5)	127.5(7)
C(11)−Ge−C(13)	118.3(5)	Ge−C(11)−C(12)	115.0(9)
C(11)−Ge−Cl	104.6(4)	Ge−C(13)−C(14)	114.8(9)

summary of cell constants and data collection parameters is included in Table 1, and the fractional coordinates and important bond lengths and angles are listed in Tables 4 and 5. A summary of important structural features is presented in Table 6.

The X-ray structure of **5** represents, to the best of our knowledge, the first structurally characterized ferrocene containing an organochlorogermanium substituent.[22] Relatively few mono- or disubstituted chlorinated ferrocenylsilanes or ferrocenylgermanes have been isolated, which may be a result of the moisture sensitivity of these compounds.[21] As for **3a**, the two cyclopentadienyl rings of **5** are nearly eclipsed and essentially planar with an observed mean deviation from the plane of 0.004 Å calculated by a weighted least squares plane through the cyclopentadienyl ligand containing C(1)−C(5), with a similar value of 0.007 Å for the cyclopentadienyl ligand containing C(6)−C(10). The most interesting feature of this structure is that the Et_2GeCl fragment is tilted toward the Fe center, rather than lying as expected in the Cp plane. The angle β between the plane of the cyclopentadienyl ligand and the ipso carbon−germanium bond is 7.5(7)°, with the chlorine atom on the face opposite the Fe center. Inspection of the unit cell diagram for **5** and nonbonded contact distances for Cl (see supplementary material) provided no obvious indication that intermolecular packing forces are responsible for the tilting of the Et_2GeCl fragment toward the iron atom. The Fe−Ge distance of 3.412(5) in **5** is far too long for a single bond (ca. 2.38−2.43 Å[18,19]) but may be indicative of a very weak iron−germanium interaction. A similar type of tilting which has been explained by an analogous interaction has been detected for ferrocenyl carbocations such as **6**.[23a,b] In this case the interaction between the iron atom and the carbocationic center of the pendent CPh_2 fragment leads to a β angle of 20.7°.[23] Significantly, if the ratio of the Fe−C_{exo} distance to the sum of the covalent radii of Fe and C for **6** (Fe−$C_{exo}/\Sigma(r_{Fe} + r_C)$ radii = 2.715 Å/1.93 Å) is compared to the analogous ratio for the ferrocenylgermane **5** (Fe−$Ge_{exo}/\Sigma(r_{Fe} + r_{Ge})$ radii = 3.412(5) Å/2.38 Å), the values are 1.41 and 1.42, respectively. This corresponds to elongations of 41% in **5** and 42% in **6** relative to single bonds, which suggests a similar bond order in each structure. To accommodate the interaction between the iron center and the Et_2GeCl fragment, the Cp rings are slightly inclined away from the organogermanium moiety, giving the molecule a small ring-tilt (α) of 4.5(9)° which is in an opposite sense to that found in **3a**. In **6** the cyclopentadienyl rings are significantly more inclined away from the exocyclic carbocationic fragment with a tilt angle (α) of 9.1°. The ring-tilt in **5** results in a less than linear Cp_{cen}−Fe−Cp_{cen} bond angle of 175.7(4)°, with the Fe center displaced slightly toward the Ge atom. Thus, the Fe atom of **5** is found 0.062(10) Å from the line joining the two centroids of the cyclopentadienyl rings. In comparison, the structure of **6** has Cp_{cen}−Fe−Cp_{cen} bond angle of 170.7° with the Fe center displaced from the line joining the two centroids by 0.08 Å. The greater tilting (α) observed for **6** in comparison to **5** is probably a consequence of the shorter (carbon−carbon) bond between the ipso carbon atom of the cyclopentadienyl ring and the carbonium center (1.416(9) Å) in the former compared to the ipso carbon−germanium bond (1.901(10) Å) in the latter. The bond lengths present in **5** are not unusual, with perhaps the exception of the Ge−Cl bond. The Ge−Cl bond length in **5** of 2.214(3) Å is significantly longer than those reported for other structures containing a Ge−Cl bond (2.067−2.148(5) Å)[24] but is nevertheless close to the sum of the covalent radii ($\Sigma(r_{Ge} + r_{Cl})$ radii = 2.21 Å).[16]

ROP of the [1]Germaferrocenophanes 3a−c. The [1]germaferrocenophane **3a** was shown to undergo rapid

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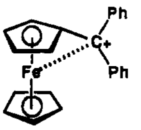
(23) (a) Behrens, U. *J. Organomet. Chem.* **1979**, *182*, 89. (b) The stabilization of α-carbocation centers by metallocenyl fragments is well known and has been reviewed. See: Koridze, A. A. *Russ. Chem. Revs.* **1986**, *55*, 113. Dative interactions between the iron center and a carbonyl group in a hydrocarbon bridge in several neutral [*m*]-ferrocenophanes have been inferred from Mössbauer and ^{13}C NMR data. See: Toma, S.; Solcaniova, E.; Nagy, A. G. *J. Organomet. Chem.* **1985**, *288*, 311. (c) Ferrocene stabilization of α-silicenium or α-germicenium cations has is not well documented. For a brief report of the cation $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4SiPh_2)]^+$ which was stable at low temperatures, see: Corey, J. Y.; Gust, D.; Mislow, K. *J. Organomet. Chem.* **1975**, *101*, C7.

(24) For simple GeX_4, Ge−Cl bond lengths in the range 2.067−2.148(5) Å have been reported. An average Ge−Cl bond length of 2.154(1) Å has been reported for the [3]ferrocenophane $Fe(\eta\text{-}C_5H_4Se)_2GeCl_2$. See: (a) Sutton, L. E. *Interatomic Distances*, Chemical Society Special Publication No. 11; The Chemical Society: London, 1958. (b) Osborne, A. G.; Blake, A. J.; Hollands, R. E.; Bryan, R. F.; Lockhart, S. *J. Organomet. Chem.* **1985**, *287*, 39, and references cited therein.

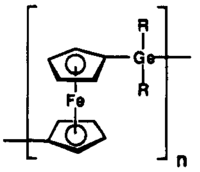
Table 6. Selected Structural Data for the [1]Ferrocenophanes 1a, 1b, 3a, and 3c, the Substituted Ferrocenylgermane 5 and the Ferrocenyl Carbocation 6 (Esd's Are in Parentheses)

	1a	1b	3a	3c	5	6
Fe–X dist, Å	2.690(3)	2.636(5)	2.804(2)	2.744(3)	3.412(5)	2.715(6)
$\Sigma(r_{Fe} + r_X)$,[a] Å	2.33	2.33	2.38	2.38	2.38	1.93
Fe displacement,[b] Å	0.2164(11)	0.183(12)	0.221(9)	0.197(14)	0.062(10)	0.080(13)
ring-tilt, α, deg	20.8(5)	19.1(10)	19.0(9)	16.6(15)	4.5(9)	9.1
β,[c] deg	37.0(6)	40.0(9)	37.7(5), 35.9(5)	38.2(8)	7.5(7)	20.7
C1–X–C6, θ, deg	95.7(4)	99.2(5)	91.7(3)	93.6(4)		
Cp–Fe–Cp, δ, deg	164.74(8)	167.3(6)	165.3(5)	166.2(7)	175.7(4)	170.7(8)
ref	4b	12	this work	11	this work	23a

[a] Sum of the covalent radii of Fe and the bridging atom X. [b] Displacement of the iron atom from the line joining the two centroids of the cyclopentadienyl rings. [c] Average of the angle(s) between the planes of the cyclopentadienyl ligands and the C(Cp)–E bonds (where E = bridging atom).

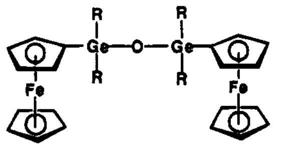


6



7

a R = Me
b R = Et
c R = Ph



8

a R = Me
b R = Et

thermal ROP at relatively low temperatures (ca. 90 °C) when heated in the melt either in a round bottom flask or in a sealed, evacuated, Pyrex tube. Thus, over 5 min at this temperature the melt became increasingly viscous and then immobile. The poly(ferrocenylgermane) product **7a** readily dissolved in THF and was isolated by precipitation into hexanes. Interestingly, the onset polymerization temperature for **3a** was 30 °C lower than that for its silicon analogue **1a**. Indeed, **3a** polymerizes so readily that significant amounts of **7a** are formed during the purification of the monomer via vacuum sublimation. Gel permeation chromatography (GPC) in THF indicated that the golden-yellow polymer **7a** derived from heating **3a** in an evacuated flask at 120 °C was of high molecular weight with a weight-average molecular weight (M_w) of 2.3 × 10^5 and a number average molecular weight (M_n) of 5.2 × 10^4. In subsequent polymerizations of **3a**, even higher molecular weight material ($M_w = 2.0 \times 10^6$, $M_n = 8.5 \times 10^5$) was obtained. The poly(ferrocenylgermane) **7a** formed flexible yellow films when cast from solvents such as THF or toluene. The ^{1}H NMR spectrum of **7a** showed the appearance of two well-resolved triplets in the cyclopentadienyl region in addition to a methyl resonance at 0.64 ppm. The ^{13}C NMR spectrum and elemental analysis data for **7a** were also consistent with the structure assigned.

The [1]ferrocenophane **3b** thermally polymerized at a slightly higher temperature than **3a** (120 °C) and a very high molecular weight polymer, **7b** ($M_w = 1.1 \times 10^6$, $M_n = 8.5 \times 10^5$), was isolated. The canary yellow powdery polymer **7b** was purified in a manner identical to that for **7a** and was characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.[25] The monomer **3c** was also observed to thermally polymerize but at a substantially higher temperature than **3a** and **3b** (230 °C). The crude product **7c** dissolved readily in THF and was precipitated from hexanes. However, after drying, the purified **7c** would not redissolve in THF but the polymer was observed to swell in very polar solvents such as DMF and DMSO. Similar insolubility and swelling behavior was previously noted for the analogous poly(ferrocenylsilane) **2b**.[3,4a] Nevertheless, characterization of **7c** before additional purification allowed the structure to be confirmed by ^{1}H and ^{13}C NMR spectroscopy.[25] In addition, GPC analysis revealed this material to be of a very high molecular weight ($M_w = 1.0 \times 10^6$; $M_n = 8.2 \times 10^5$).

Reaction of 3a and 3b with Moisture: Isolation of the Bis(ferrocenyl)germoxanes 8a and 8b. The strained species **3a** and **3b** were also found to be sensitive to moisture and readily afforded the germoxanes **8a** and **8b** when exposed to the atmosphere. Kumuda previously prepared the dimethyl derivative **8a** via the acid hydrolysis of the ferrocenyldigermane $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)GeMe_2GeMe_3$.[26] The bis(ferrocenyl)germoxanes **8a** and **8b** were readily identified by ^{1}H and ^{13}C NMR as well as by mass spectrometry and elemental analysis. The formation of **8a** and **8b** from **3a** and **3b** is similar to generation of bis(ferrocenyl)titanoxanes reported by Gautheron and co-workers via the exposure of [1]ferrocenophanes containing a bridging Ti atom to atmospheric moisture.[27]

Summary

The germanium-bridged [1]ferrocenophanes **3a–c** have been synthesized, and their polymerization behavior studied. The X-ray diffraction study of **3a** confirmed that this species possesses a highly strained, ring-tilted structure and that a weak dative interaction between iron and germanium is present. Structural and Mössbauer data for this species suggest that this interaction is weaker than in the case of the phenylated analogue **3c**. The ferrocenylgermane **5** also appears to possess a very weak interaction between the iron center and the germanium atom which is analogous to that detected in ferrocene-stabilized carbocations such as **6**. The germanium-bridged [1]ferrocenophanes **3a–c** undergo thermally induced ROP when heated in the melt to yield the poly(ferrocenylgermanes) **7a–c**. Work is currently underway aimed at answering detailed questions about the ROP mechanism for germanium-bridged [1]ferrocenophanes and related species. We are also currently investigating the properties of poly(ferrocenylgermanes)

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(25) Elemental analysis data for the polymers **7b** and **7c** were found to be in reasonable agreement with the assigned structures for hydrogen, but the values for carbon were found to be slightly low (between 0.5 and 0.8%) even after repeated analyses on spectroscopically pure samples. We attribute the low carbon values to incomplete combustion due to the formation of ceramic products at elevated temperatures. Similar behavior has been found for poly(ferrocenylsilanes) (see refs 4a–c,e).

(26) Kumada, M.; Kondo, T.; Mimura, K.; Yamamoto, K.; Ishikawa, M. *J. Organomet. Chem.* **1972**, *43*, 307.

(27) Broussier, R.; Da Rold, A.; Gautheron, B.; Dromzee, Y.; Jeannin, Y. *Inorg. Chem.* **1990**, *29*, 1817.

and we recently reported electrochemical studies which showed that the iron centers in **7a** interact with one another in a similar manner to those in poly(ferrocenylsilanes) **2**.[4d] The results of our studies in the areas of both polymerization mechanisms and polymer structure/property relations will be the subjects of future publications.

Experimental Section

Materials. Ferrocene, 1.6 M butyllithium in hexanes, and tetramethylethylenediamine (TMEDA) were purchased from Aldrich. *Diethyldichlorogermane and diphenyldichlorogermane* were purchased from Geleste and were used as received. The dimethyldichlorogermane, which was distilled prior to use, was generously donated by Prof. Robert Morris.

Equipment. All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Vacuum Atmospheres), except for the polymer manipulations which were carried out in air. Solvents were dried by standard methods, distilled, and stored under nitrogen over activated molecular sieves. The 200 or 400 MHz ^{1}H NMR spectra and 50.3 or 100.5 MHz ^{13}C NMR spectra were recorded either on a Varian Gemini 200 or Varian Unity 400 spectrometer. Room temperature ^{57}Fe Mössbauer spectra were obtained using a Ranger Scientific Inc. Vt-1200 instrument using a MS-1200 digital channel analyzer. The γ-ray source was a 6 mCi ^{57}Co sample supplied by Amersham. The data were collected in a -15.8 mm s^{-1} to $+15.8$ mm s^{-1} range and referenced to Fe foil. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer operating in either an electron impact (EI) or fast atom bombardment (FAB) mode. Molecular weights were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a Model 510 HPLC pump, a Model U6K injector, and a Ultrastyragel columns differential refractometer. A flow rate of 1.0 mL/min was used, and the eluent was a solution of 0.1% tetra-*n*-butylammonium bromide in THF. Polystyrene standards were used for calibration purposes. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

Synthesis of the [1]Germaferrocenophanes 3a–c. The compounds **3a–c** were prepared by slight modifications of the method reported by Wrighton[14b] and Osborne[14a] for the synthesis of the silicon-bridged [1]ferrocenophanes **1a** and **1b**. The syntheses for **3a–c** monomers were similar, and only the procedure for **3a** is therefore given. Compounds **3a–c** were isolated as red-orange crystalline materials in 26% (**3a**), 35% (**3b**), and 30% (**3c**) yields, respectively, after purification by high-vacuum sublimation (50–150 °C, 0.005 mmHg). The previously reported compound **3c** was identified by ^{1}H NMR spectroscopy.

Synthesis of 3a. To dilithioferrocene·TMEDA (3.2 g, 10.2 mmol) in diethyl ether (150 mL) at -78 °C was added a cooled (-78 °C) solution of Me_2GeCl_2 (1.79 g, 10.2 mmol) in diethyl ether (25 mL) over 30 min using a double tip needle. The reaction mixture was slowly allowed to warm to room temperature over 3 h and was then stirred overnight. The reaction mixture was then filtered and the solvent removed. Residual TMEDA was then removed under vacuum (25 °C, 0.005 mmHg). The dark red tacky residue was then sublimed twice (50 °C, 0.01 mmHg) to yield the red-orange crystalline product. Yield 0.75 g (26%), mp 90 °C.

Data for 3a. ^{13}C NMR (in C_6D_6) $\delta = 76.9$ (Cp), 75.9 (Cp), 31.0 (ipso-Cp), -3.3 (CH_3) ppm. ^{1}H NMR (in C_6D_6) $\delta = 4.39$ (pseudo tr; $^3J_{HH} = 1.6$, 4H, Cp), 4.03 (pseudo tr; $^3J_{HH} = 1.6$, 4H, Cp), 0.46 (s, 6H, CH_3) ppm. MS (EI, 70 eV): *m/z* (rel intensity) = 288 (100, M$^+$), 273 (37, M$^+$ − CH_3), 258 (36, M$^+$ − $2CH_3$). HRMS $C_{12}H_{14}{}^{74}Ge^{56}Fe$ calcd 287.9657, exp 287.9660. Anal. Calcd: C, 50.27; H, 4.92. Found: C, 50.49; H, 5.01. Mp 90 °C.

Data for 3b. ^{13}C NMR (in C_6D_6) $\delta = 76.8$ (Cp), 76.4 (Cp), 30.0 (ipso-Cp), 8.71 (CH_2CH_3), 5.55 (CH_2CH_3) ppm. ^{1}H NMR (in C_6D_6) $\delta = 4.30$ (pseudo tr; $^3J_{HH} = 1.6$, 4H, Cp), 4.05 (pseudo tr; $^3J_{HH} = 1.6$, 4H, Cp), 1.15 (m, 6H, CH_2CH_3), 1.13 (m, 4H, CH_2CH_3) ppm. MS (EI, 70 eV): *m/z* (rel intensity) = 316 (100, M$^+$), 287 (9, M$^+$ − CH_2CH_3), 259 (92, M$^+$ − $2CH_2CH_3$ + 1). HRMS $C_{14}H_{18}{}^{74}Ge^{56}Fe$ calcd 315.9970, exp 315.9952. Anal. Calcd: C, 53.43; H, 5.76. Found: C, 52.77; H, 5.77. Mp 85 °C.

Data for 3c. ^{1}H NMR (in C_6D_6) $\delta = 7.85$–7.81 (m; 4H, *o*-Ph), 7.23–7.18 (m; 6H, *m*- and *p*-Ph), 4.37 (pseudo tr; $^3J_{HH} = 1.7$, 4H, Cp), 4.18 (pseudo tr; $^3J_{HH} = 1.7$, 4H, Cp) ppm. MS (EI, 70 eV): *m/z* (rel intensity) = 412 (100, M$^+$), 335 (21, M$^+$ − C_6H_5). HRMS $C_{22}H_{18}{}^{74}Ge^{56}Fe$ calcd 411.9970, exp 411.9983. Note: no melt was observed for a crystalline sample of **3c** by DSC, which was consistent with the literature report for this compound.[11]

Synthesis of the Ferrocenylgermane 5. To a cool ether (0 °C) solution containing $Fe(\eta\text{-}C_5H_4HgCl)(\eta\text{-}C_5H_5)$[15] (1.0 g, 2.4 mmol) was added 2 equiv of *n*-BuLi, followed by the addition at room temperature of Et_2GeCl_2 (0.48 g, 2.4 mmol). After 12 h, filtration to first remove LiCl, followed by high-vacuum distillation to remove ether and Hg(*n*-Bu)$_2$, lead to the isolation of a golden-brown liquid at room temperature in 65% yield (0.55 g, 1.56 mmol). Golden crystals (mp = 25 °C) were obtained from the recrystallization of **5** from hexanes (0 °C). Compound **5** was also isolated as a 10% impurity from the initial synthesis of **3b**. This species was identified by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, elemental analysis, and finally by an X-ray diffraction study.

Data for 5. ^{13}C NMR (in C_6D_6) $\delta = 72.7$ (Cp), 71.3 (ipso-Cp), 71.2 (Cp), 68.9 (η-C_5H_5), 12.3 (CH_2CH_3), 8.6 (CH_2CH_3) ppm. ^{1}H NMR (in C_6D_6) $\delta = 4.13$ (pseudo tr; $^3J_{HH} = 1.6$, 2H, Cp), 4.04 (pseudo tr; $^3J_{HH} = 1.6$, 2H, Cp), 4.01 (s, 5H, η-C_5H_5), 1.13 (m, 10H, CH_2CH_3) ppm. MS (EI, 70 eV): *m/z* (rel intensity) = 352 (100, M$^+$), 323 (64, M$^+$ − CH_2CH_3), 294 (66, M$^+$ − $2CH_2CH_3$), 259 (23, M$^+$ − $2CH_2CH_3$ − Cl). HRMS $C_{14}H_{19}{}^{35}Cl^{74}Ge^{56}Fe$ calcd 351.9736, exp 351.9746. Anal. Calcd: C, 47.88; H, 5.45; Cl, 10.10. Found: C, 47.69; H, 5.44; Cl, 9.83. Mp 25 °C.

Synthesis of the Poly(ferrocenylgermanes) 7a–c via Thermal ROP in the Melt. The syntheses of the polymers **7a–c** from the monomers **3a–c** were similar, and only the procedure for **7a** is therefore given. Polymers **7b** and **7c** were prepared at 120 and 230 °C, respectively.

Synthesis of the Poly(ferrocenylgermane) 7a. In a typical experiment a sample of **3a** (1.5 g, 8.3 mmol) was heated under vacuum in a round bottom flask at 120 °C. A marked increase in viscosity was observed and after 5 min the flask contents were immobile. The polymeric product was dissolved in THF (10 mL) over 24 h and the filtered solution added slowly, dropwise, to stirred hexanes (500 mL). After allowing the polymer to settle out, the mother liquors were decanted. The yellow, fibrous material was then dried in vacuo. The yield was 1.2 g (80%).

Polymers **7a–c** were isolated as yellow powders in 80% (**7a**), 85% (**7b**), and 90% (**7c**) yields, respectively.

Slightly lower molecular weight samples of these materials were also formed via ROP in the purification of **3a–c** during the thermal treatment in the sublimation step. Similar behavior has been previously noted for silicon-bridged [1]-ferrocenophanes such as **1** (R = *n*-Hex).[4a]

Data for 7a. ^{13}C NMR (in C_6D_6) $\delta = 74.6$ (ipso-Cp), 72.9 (Cp), 71.0 (Cp), -1.1 (CH_3) ppm. ^{1}H NMR (in C_6D_6) $\delta = 4.25$ (pseudo tr; $^3J_{HH} = 1.6$ Hz, 4H, Cp), 4.11 (pseudo tr; $^3J_{HH} = 1.6$ Hz, 4H, Cp), 0.64 (s, 6H, CH_3) ppm. Anal. Calcd: C, 50.27; H, 4.92. Found: C, 50.30; H, 4.87. GPC: 1st sample, $M_w = 2.3 \times 10^5$; $M_n = 5.2 \times 10^4$, 2nd sample, $M_w = 2.0 \times 10^6$; $M_n = 8.5 \times 10^5$.

Data for 7b. ^{13}C NMR (in C_6D_6) $\delta = 73.3$ (Cp), 73.0 (ipso-Cp), 71.1 (Cp), 9.9 (CH_2CH_3), 7.6 (CH_2CH_3) ppm. ^{1}H NMR (in C_6D_6) $\delta = 4.30$ (s; 4H, Cp), 4.13 (s; 4H, Cp), 1.27 (m, 10 H,

CH_2CH_3) ppm. Anal. Calcd: C, 53.43; H, 5.76. Found: C, 52.63; H, 5.77. GPC: 1st sample, $M_w = 3.4 \times 10^4$; $M_n = 8.6 \times 10^3$, 2nd sample, $M_w = 1.0 \times 10^6$; $M_n = 8.1 \times 10^5$. From 0.80 g (2.5 mmol) of **3b** a 0.68 g yield of **7b** (85%) was obtained.

Data for 7c. ^{13}C NMR (in C_6D_6) δ = 139.8 (Ph$_{ipso}$), 139.8 (*o*-Ph), 129.0 (*p*-Ph), 128.5 (*m*-Ph), 75.6 (Cp$_{ipso}$), 74.0 (Cp), 70.8 (Cp) ppm. ^{1}H NMR (in C_6D_6) δ = 7.75 (br s; 4H, *o*-Ph), 7.25 (br m, 6 H, *m*-, *p*-Ph), 4.28 (br s; 4H, Cp), 4.15 (br s; 4H, Cp) ppm. Anal. Calcd: C, 64.32; H, 4.42. Found: C, 63.79; H, 4.42. GPC: $M_w = 1.0 \times 10^6$; $M_n = 8.2 \times 10^5$. From 0.5 g (1.2 mmol) of **3c** a 0.45 g yield of **7c** (90%) was obtained.

Synthesis of the Bis(ferrocenyl)germoxanes 8a and 8b. When the isolated monomers **3a** or **3b** (0.2 g) were exposed to moist air (12 h), the red-orange crystalline [1]germaferrocenophanes were slowly converted, quantitatively, to the corresponding yellow crystalline germoxanes **8a** and **8b**. Similar reactions occurred in solutions that were exposed to air. However, in this case the yield of the germoxanes **8a** and **8b** is less due to competitive formation of poly(ferrocenylgermanes) **7a** and **7b**. The germoxane **8a** was previously prepared by Kumada via the alcoholysis of monosubstituted ferrocenyldigermanes and this species was previously characterized by ^{1}H NMR and elemental analysis.[26] Additional data are provided here for completeness.

Data for 8a. ^{13}C NMR (in C_6D_6) δ = 74.7 (ipso-Cp), 72.9 (Cp), 70.8 (Cp), 68.6 (η-C_5H_5), 2.2 ppm (CH_3). ^{1}H NMR (in C_6D_6) δ = 4.16 (pseudo tr; $^3J_{HH}$ = 1.7 Hz, 4H, Cp), 4.05 (pseudo tr; $^3J_{HH}$ = 1.7 Hz, 4H, Cp), 3.95 (s, 10H, η-C_5H_5), 0.53 (s, 12H, CH_3) ppm. MS (EI, 70 eV): *m/z* (rel intensity) = 592 (100, M$^+$), 527 (14, M$^+$ − Cp), 391 (76, M$^+$ − Fc − CH_3 + 1). HRMS $C_{24}H_{30}O^{74}Ge_2{}^{56}Fe_2$ calcd 593.9419, exp 593.9428. Mp 117 °C.

Data for **8b.** ^{13}C NMR (in C_6D_6) δ = 73.5 (ipso-Cp), 73.2 (Cp), 70.5 (Cp), 68.6 (η-C_5H_5), 10.5 (CH_2CH_3), 8.74 (CH_2CH_3) ppm. ^{1}H NMR (in C_6D_6) δ = 4.17 (pseudo tr; $^3J_{HH}$ = 1.7 Hz, 4H, Cp), 4.07 (pseudo tr; $^3J_{HH}$ = 1.6 Hz, 4H, Cp), 4.02 (s, 10H, η-C_5H_5), 1.25 (m, 12H, CH_2CH_3), 1.06 (m, 8H, CH_2CH_3) ppm. MS (EI, 70 eV): *m/z* (rel intensity) = 648 (90, M$^+$), 433 (100, M$^+$ − Fc − CH_2CH_3 + 1), 404 (17, M$^+$ − Fc − 2CH_2CH_3 + 1), 334 (92, M$^+$ − Fc − Ge − 2CH_2CH_3 − 1). HRMS $C_{28}H_{38}O^{74}Ge_2{}^{56}Fe_2$ calcd 650.0045, exp 650.0084. Anal. Calcd: C, 51.94; H, 5.92. Found: C, 51.78; H, 5.83. Mp 55 °C.

X-ray Structure Determination Technique. Crystals of **3a** and **5** used for this analysis were each mounted on a glass fiber and coated with epoxy glue. Both crystals had dimensions in the range of 0.25−0.45 mm. Intensity data for the compounds **3a** and **5** were collected on an Enraf-Nonius CAD-4 diffractometer at 193 and 173 K, respectively, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The $\omega-2\theta$ scan technique was applied with variable scan speeds. Intensities of three standard reflections were measured every 2 h. This showed no decay in the case of **3a**. The data for **5** were corrected for a linear intensity decay of 35%. An empirical absorption correction was applied in both cases (maximum and minimum corrections 1.208, 0.762 for **3a** and 1.140, 0.724 for **5**).[28]

The positions of the non-hydrogen atoms for both **3a** and **5** were determined by direct methods using Siemens SHELXTL PC.[29] For both structures all non-hydrogen atoms were refined anisotropically by full-matrix least squares to minimize $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F_o) + gF_o{}^2$. For compounds **3a** and **5** the hydrogen atoms were included in calculated positions (C−H 0.96 Å). Crystal data, details of data collection, and least squares parameters are listed in Tables 1−6. Figures 1 and 2 are views of the molecules prepared using SHELXTL PC. Atomic scattering factors were taken from ref 30. All calculations were carried out on a PC-486.

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Supplementary Material Available: Tables of complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, and least-squares plane data and figures showing the molecular structures of **3a** and **5** (17 pages). Ordering information is given on any current masthead page.

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