# Novel Ceramic and Organometallic Depolymerization Products from Poly(ferrocenylsilanes) *via* Pyrolysis

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When heated at 500 °C under nitrogen the poly(ferrocenylsilanes) $[Fe(\eta\text{-}C_5H_4)_2(SiR_2)]_n$ (**1**; R = Me, or **2**; R = Ph) yield magnetic iron silicon carbide ceramics together with a orange–yellow sublimate which, in the case of **1**, was shown to contain the unusual unsymmetrical dimer $[Fe(\eta\text{-}C_5H_4)_2(\mu\text{-}SiMe_2)_2(\eta\text{-}C_5H_3)Fe(\eta\text{-}C_5H_5)]$ **3** by single crystal X-ray diffraction.

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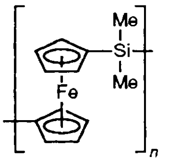
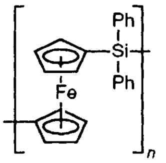
Macromolecules containing inorganic elements are of considerable interest as pyrolytic precursors to ceramics.[1] This is a consequence of the intimate atomic-scale mixing present in a polymer which should promote the facile formation of 3D extended structures and the unique processing advantages of polymers which allows the preparation of high-performance nonmetallic structural ceramic objects, fibres and coatings.[1] To date, most studies have concentrated on the use of polymers as precursors to structural ceramics with outstanding mechanical properties such as silicon carbide, silicon nitride and boron nitride.[1] By contrast, the use of polymers as precursors to transition metal-containing solid state materials, which are known to possess a wide range of interesting electrical, magnetic and optical properties, is virtually unexplored.[1,2] In this paper we report some of our initial studies on the pyrolysis of high molecular weight poly(ferrocenylsilanes) which were synthesized recently by our group *via* a novel ring-opening route.[3,4] In particular, we show that these polymers function as pyrolytic precursors to both interesting transition metal containing ceramics and novel organometallic depolymerization products.

The poly(ferrocenylsilanes) **1** and **2** were prepared *via* the thermal ring-opening polymerization of the corresponding [1]ferrocenophane precursors in the melt at 120–220 °C.[3]† Analysis of the thermal stability of **1** and **2** by thermogravimetric analysis (TGA) indicated that the polymers undergo significant weight loss at 350–500 °C to afford ceramic residues in *ca.* 35–40% yield with no further weight loss up to 1000 °C (scan rate 10 °C $min^{-1}$ under $N_2$). When either **1** or **2** was heated in a tube furnace at 500 °C for 6 h under a slow flow of dinitrogen a lustrous, ceramic product was formed together with an orange–yellow sublimate which condensed on the cooler sections of the quartz tube.



**1**



**2**

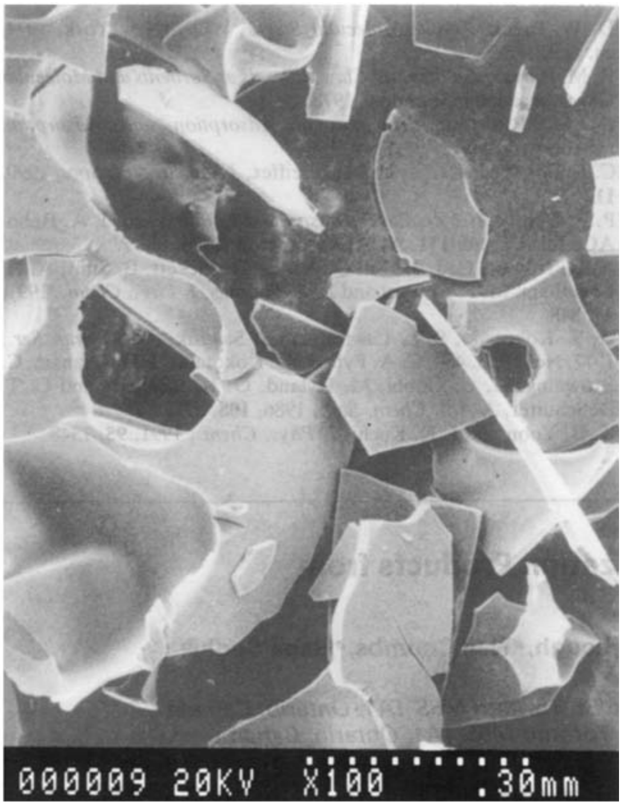


**Fig. 1** A scanning electron micrograph of the ceramic derived from **2** (100× magnification)

The ceramic products, which were readily attracted to a bar magnet at room temperature, were characterized by scanning electron microscopy (SEM) with backscattered electron imaging (BEI) and energy dispersive X-ray (EDX) microanalysis, and by X-ray photoelectron spectroscopy (XPS). An illustrative scanning electron micrograph of the material derived from **2** is shown in Fig. 1. The ceramic derived from **1** showed no signs of crystallinity such as the presence of grain boundaries or facetted surfaces by high resolution SEM even at $10^5$ magnification. Moreover, high resolution BEI indicated that the material was uniform with no dramatic segregation of elements on a scale greater than 30 nm. EDX analysis was carried out using a sample of polymer **1** as a compositional standard and indicated the presence of iron, silicon and carbon in an approximate‡ ratio of 30 : 17 : 53, together with trace amounts of oxygen. Similar characteristics and a similar composition were noted for the ceramic derived from polymer **2**. Analysis of the topmost surfaces of the ceramics derived from **1** and **2** by XPS indicated that the major constituent was carbon, with significant amounts of oxygen, small amounts of silicon and very small quantities of iron.§ X-Ray powder diffraction studies confirmed that ceramics derived from both **1** and **2** are completely amorphous.

In the case of polymer **1** the yellow–orange sublimate formed during the pyrolysis was dissolved in $CH_2Cl_2$ and was then chromatographed on a silica gel column. Elution with hexanes yielded an orange band which afforded crystals of a compound **3**, the mass spectrum of which showed a molecular ion at *m*/*z* 484 consistent with a product containing two ferrocenyldimethylsilane units. Analysis of **3** by single crystal X-ray diffraction indicated that this species possessed a novel structure in which the two organosilicon substituents bonded

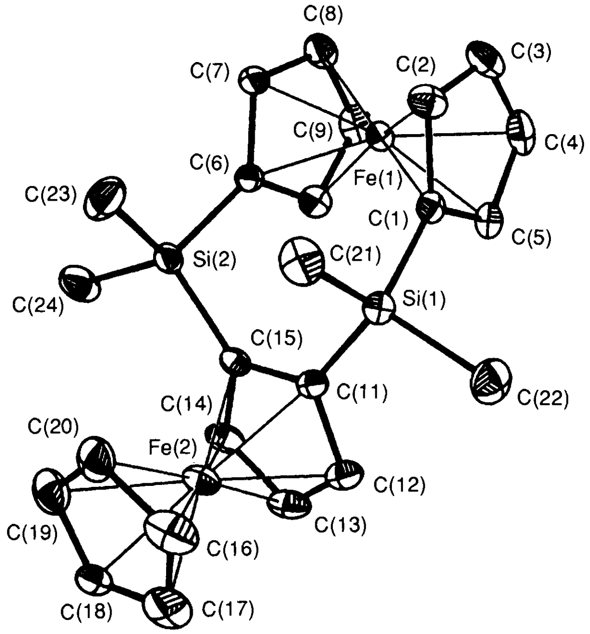


**Fig. 2** The molecular structure of **3** (with thermal ellipsoids at the 25% probability level)

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† For polymer **1** gel permeation chromatography (relative to polystyrene standards) gave $M_w = 5.2 \times 10^5$, $M_n = 3.4 \times 10^5$. High molecular weight samples of polymer **2** are insoluble in organic solvents. However, based on the molecular weights of soluble fractions of **2** extracted with hot tetrahydrofuran lower limits are $M_w = 5.1 \times 10^4$, $M_n = 3.2 \times 10^4$.

‡ The errors for the EDX analysis are estimated as *ca.* ±5% for Fe and Si and ±10% for C.

§ The XPS data are based on integration of the following peaks: Fe (2p3/2, 708.1 eV), Si (2p, 102.4 eV), C (1s, 284.6 eV), O (1s, 532.4 eV). Composition of ceramic derived from **1**: Fe 0.8, Si 5.1, C 79.6, O 14.5%. For ceramic derived from **2**: Fe 2.0, Si 6.0, C 85.7, O 6.3%. The origin of the oxygen present is currently under investigation. It may arise from traces of dioxygen in the atmosphere during the pyrolysis or from exposure of the ceramic to the air during the work up.

to one ferrocenyl moiety are also attached to a single cyclopentadienyl ligand of another leaving the other cyclopentadienyl ligand unsubstituted (Fig. 2).¶ The mechanism of formation of this surprising compound is as yet unknown although clearly a silicon–hydrogen atom exchange at one cyclopentadienyl ligand must be involved at some stage.

Further work is directed towards the full characterization of both the volatile and ceramic products derived from poly(ferrocenylsilanes) with particular emphasis on understanding the nature and origin of the magnetism in the latter. In addition, we are attempting to elucidate the mechanism of formation of **3** in order to design related polymers in which depolymerization is minimized and the corresponding ceramic yield is increased.

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¶ *Crystal data* for **3**. $C_{24}H_{28}Fe_2Si_2$, $M_r$ = 484.3, monoclinic space group $P2_1/c$, $Z = 2$, $a$ = 9.3842(2), $b$ = 15.455(2), $c$ = 15.6630(12) Å, $\beta$ = 91.092(6)°, $V$ = 2271.2(11) Å$^3$, $D_c$ = 1.42 g cm$^{-3}$, $\lambda$(Mo-K$\alpha$) = 0.71073 Å, $\mu$ = 13.9 cm$^{-1}$, $F(000)$ = 1008, $T$ = 294 K. Accurate cell dimensions and the crystal orientation matrix were determined on a CAD4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $10 < \theta < 15°$. 3009 reflections were measured ($2 < 2\theta < 46°$), 2998 unique ($R_{int}$ = 0.018) and 2580 with $I > 3\sigma(I)$ were used in the calculations. Data were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by direct methods using SHELXTL PC (G. M. Sheldrick, SHELXTL PC, 1990, Siemens Analytical X-ray Instruments, Inc., Karlsruhe, Germany). Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters for Si, Fe and C atoms. Hydrogen atoms were positioned on geometric grounds (C–H 0.96 Å) and included (as riding atoms) in the structure factor calculation. A general hydrogen atom thermal parameter was refined, final value $U_{iso}$ 0.084(1) Å$^3$. Final cycle of least-squares refinement included 281 parameters and gave $R$ = 0.028, $R_w$ = 0.031, and goodness of fit 2.02 [$Iw = 1/(\sigma^2(F_o) + 0.0001(F_o)^2]$. Maximum density in the final difference map was in the range −0.28 to 0.22 e Å$^{-3}$. The free $\eta$-$C_5H_5$ cyclopentadienyl ring was found to be disordered with half occupancy of the carbon atoms in the eclipsed and staggered conformations. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.