Organometallics **2001,** *20,* 4211−4215 4211

X-ray Structure of a Novel Tetrachloro[1.1]silaferrocenophane. Hydrolysis−Polycondensation of Poly(ferrocenyldichlorosilane). Electrochemical Studies

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Received December 5, 2000

The thermal ring-opening polymerization of 1,1′ferrocenediyldichlorosilane (**m1**) led to the expected poly(ferrocenyldichlorosilane) (**p1**) and the new dimer **d1**. The molecular structure of **d1** was established by X-ray crystallography, and the electrochemical behavior was indicative of an electronic interaction between the ferrocene units. The hydrolytic sol−gel polycondensation of **p1** led to a material in which the polymer chain was preserved during the process, as shown by the cyclic voltammetry study.

Introduction

Over the past few decades, polymers containing transition metals in the main chain have attracted considerable attention due to their physical (redox, magnetic, electrical, etc.) and chemical properties.[1] In the field of nanostructured organic−inorganic materials obtained by sol−gel routes, it is possible to introduce organic or organometallic moieties into a silica matrix.[2−8] In these solids the organic or organometallic units are covalently bound to the matrix and the properties of the molecular organic or organometallic moiety generally are preserved.[9−15] To confirm the generality of this observation, we have been particularly interested in a class of organometallic polymers described recently,[1] which contain ferrocene units in the chain. They are very attractive, since the authors[16−21] reported a very specific redox cooperation between the iron centers along the polymer backbone, showing a highly characteristic two-wave cyclic voltammogram. It would be very interesting to follow the presence and the possible evolution of this very specific property in the solid. We have recently described the first results obtained in this field and, in particular, a route to 1,1′-ferrocenediyldialkoxysilanes involving 1,1′-ferrocenediyldichlorosilane (**m1**) as an intermediate.[22] Recently, ring-opened poly(ferrocenylsilanes) with alkoxy, aryloxy, and amino substituents at silicon have been reported.[23,24] In this context, we report here that the thermal ring-opening reaction of monomer **m1** leads to the expected poly-

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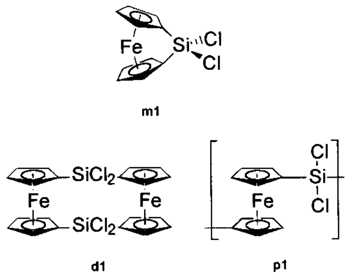
Chart 1



(ferrocenyldichlorosilane) (**p1**) and to the new dimer **d1**. The single-crystal X-ray diffraction study of this dimer is described and correlated to its electrochemical behavior. The hydrolytic polycondensation of polymer **p1** afforded a new hybrid organic–inorganic solid, **Gp1H**, in which the polymer chain is preserved, as demonstrated by a cyclic voltammetry study.

Results and Discussion

The red, crystalline 1,1′-ferrocenediyldichlorosilane (**m1**) was prepared via the reaction of 1,1′ dilithioferrocene/TMEDA with $SiCl_4$.[25] The ^1H, ^{13}C, and ^{29}Si NMR chemical shift values were found to be in good agreement with those previously reported.[25,26] The synthesis of poly(ferrocenyldichlorosilane) (**p1**) was investigated by the route previously described by Manners and coworkers.[26] However, an orange-red, crystalline compound was formed during the thermal treatment of pure **m1** and was separated from the polymer **p1**. This unknown compound was identified as the dimer **d1** (Chart 1). A tetramethylated analogue has been reported,[27,28] and more recently, oligomeric species (dimer, trimer) have been observed during the thermal ring-opening polymerization of 1,1′-ferrocenediyldiferrocenylsilane.[29] The dimer **d1** was characterized by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy in CD_2Cl_2 solution. The signals corresponding to the hydrogen atoms of the cyclopentadienyl rings appeared at 4.2 and 4.7 ppm. The ^{13}C NMR spectrum showed three characteristic signals due to the monosubstituted cyclopentadienyl rings. It is interesting to compare the spectra of **d1** and **m1**. A large shift of the ipso carbon atom signal from 36.1 ppm in the strained 1,1′-ferrocenediyldichlorosilane **m1** to 70.1 ppm in **d1** was observed. In the same way, the ^{29}Si NMR chemical shift varied from −4.8 ppm for **m1** to 12.5 ppm in the case of **d1**. Similar results have been described in the case of the tetramethylated dimer analogue and are attributed to the loss of constraint along the Si–C bond.[27,28]

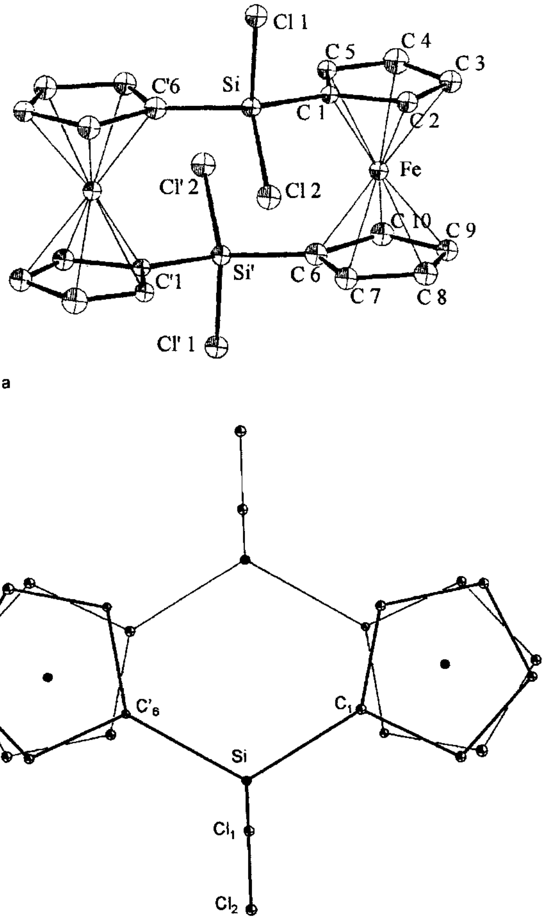


Figure 1. (a) ZORTEP drawing of the molecule **d1** with ellipsoids at the 30% probability level. (b) Alternate view of **d1** with thermal ellipsoids reduced to a 5% probability level in order to minimize atom overlaps.

Table 1. Summary of Crystal Data and Intensity Measurement and Refinement Details for Compound d1

formula	$C_{10}H_8Cl_2FeSi$
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	6.956(3)
b, Å	13.691(3)
c, Å	10.910(3)
β, deg	90.95(3)
V, A^3	1038.9(5)
mol wt	283.01
Z	4
d_{calcd}, g cm^{-3}	1.810
cryst size, mm^3	0.25 × 0.10 × 0.03
cryst color	orange-red
mp, °C	>220, dec
method of data collecn	ω,θ
radiation (graphite monochromated)	Mo Kα
μ, cm^{-1}	20.35
2θ limits, deg	4–60
no. of unique rflns	2606
no. of obsd rflns	729
final no. of variables	118
R1 for 729 $F_o > 4\sigma(F_o)$	0.0784
wR2 (on F^2)	0.2272
GOF	0.794
residual electron density	0.98 (−0.74)

The molecular structure of **d1** was established by X-ray crystallography (Figure 1). Data collection parameters for **d1** are reported in Table 1. The molecule is centrosymmetric and closely resembles 1,1,12,12-tetramethyl[1,1]-silaferrocenophane.[27,28] The four centers of the cyclopentadienyl rings define rigorously a plane from which the iron atoms are slightly lying apart (0.023 Å). The Fe···Fe distance is 5.930 Å. The iron–

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Table 2. Bond Lengths and Fe−Fe′ Interatomic Distances in Å

Fe−C (av)	2.042(11)	Si−C6′	1.820(12)
C−C (av)	1.415(16)	Si−Cl1	2.060(5)
Si−C1	1.837(12)	Si−Cl2	2.041(5)
Fe⋯Fe′	5.930		

Table 3. Main Angles in deg

C1−Si−C6′	118.0(6)	Si−C1−C5	128.5(9)
C1−Si−Cl1	105.7(4)	C2−C1−C5	105.2(11)
C1−Si−Cl2	111.2(4)	Si′−C6−C7	122.7(9)
Cl1−Si−Cl2	104.0(2)	Si′−C6−C10	132.5(10)
C6′−Si−Cl1	105.7(4)	C7−C6−C10	104.3(10)
C6′−Si−Cl2	111.0(5)	Cp−Fe−Cp	175.1
Si−C1−C2	126.1(9)	Cp∧Cp (dihedral)	3.5

carbon distances range from 2.02(1) to 2.07(1) Å, with an average distance of 2.04 Å.

The interplanar angle between the two Cp rings of each ferrocenyl moiety is only 3.5°. Here a larger value (4.9°) is found for the "deviation from the straight line" given by the Cp−Fe−Cp angle of 175.1°. The two rings tend to be moderately eclipsed, since the average staggering angle is 15.1°. This value compares with those observed (13.6°[27] and 13.2°[28]). Actually this staggering angle value seems to result from a balance with several other angle strains. We think that the geometry of the $SiCl_2$ (or $SiMe_2$) groups bridging the two ferrocenyl moieties, best shown in Figure 1b, is likely to modify mainly such constraints. Minor changes are to be expected for the angles around the carbon atoms C1 and C6. However, the bond lengths Si−C1 = 1.84(1) Å and Si−C6 = 1.82(1) Å are reduced in comparison with the Si−C values of 1.861(3) and 1.865(9) Å reported, respectively, in refs 27 and 28. Moreover, a larger Cp−Si−Cp angle is observed for **d1**, 118.0(6)°, as compared with 112.9(1)° [27] and 113.0(4)°.[28] An examination of Figure 1 shows that increasing the value of the C1−Si−C6 angle would be in accordance with a *more staggered* ferrocene; on the other hand, low values of this angle would fit the geometry of a *more eclipsed* ferrocene moiety. Only a minor amount of strain seems to occur in the molecule of **d1**, since the Si atom lies only 0.28 Å apart from the Cp ring mean plane, thus defining a bending angle of ca. 8.7° opposite to the Fe atom. Selected bond distances (Å) and angles (deg) are given in Tables 2 and 3, respectively.

Hydrolysis−Polycondensation of p1. The dark amber, hard solid **p1**, which is an insoluble material, was suspended in THF in the presence of triethylamine and treated with 10 equiv of water under an argon atmosphere. Rapidly, the reaction mixture became orange. The reaction mixture was stirred for 16 h. The orange solid formed was ground in a mortar to a powder and washed with water, acetone, and diethyl ether. **Gp1H** was isolated as an insoluble orange powder and was characterized by NMR spectroscopy. The ^{13}C CPMAS NMR spectrum of **Gp1H** showed one broad resonance at 73 ppm attributable to the cyclopentadienyl carbon atoms. The ^{29}Si CPMAS NMR spectrum of **Gp1H** exhibited a sharp signal at −29 ppm assigned to substructures of type D ($C_2Si(OSi)_2$).[30] These data appeared to be very similar compared to the solids obtained by hydrolytic polycondensation of dialkoxysilyl analogues.[22]

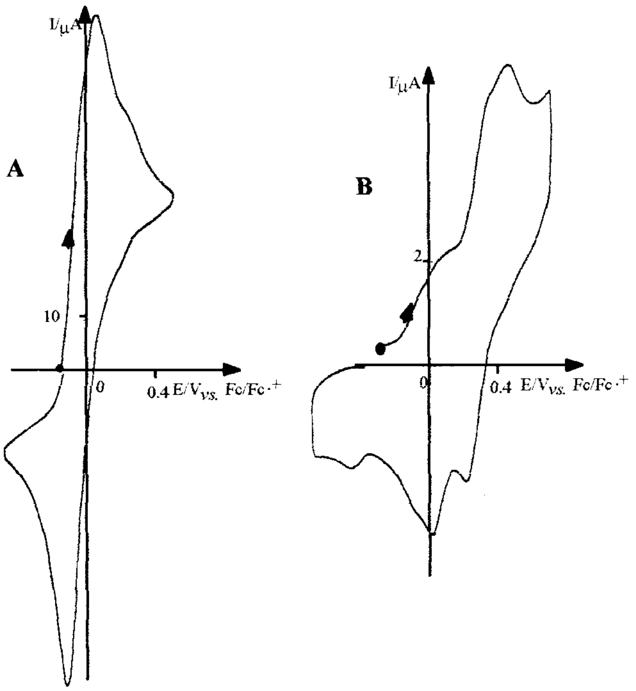

Figure 2. Cyclic voltammogram (100 mV s^{-1}) of (A) monomer **m1** in a freshly prepared solution and (B) dimer **d1**. The electrolyte is dried acetonitrile containing TBAP (0.1 M). The working electrode is a glassy-carbon electrode (diameter 3 mm). The potentials are referenced to the potential of the ferrocene/ferrocenium redox system.

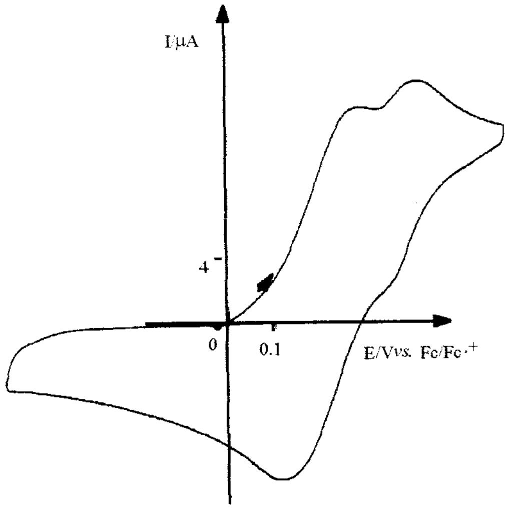

Figure 3. Cyclic voltammogram (100 mV s^{-1}) of a platinum electrode (diameter 5 mm) modified by a composite film of **Gp1H** and PTFE. Other conditions are as in Figure 2.

Electrochemical Study. Monomer **m1** and dimer **d1** are extremely sensitive to moisture in the air, and electrochemical experiments were performed under a dried argon atmosphere in a glovebox with carefully dried acetonitrile containing 0.1 M TBAP (tetra-*n*-butylammonium perchlorate). Even so, electrolytic solutions of **m1** and **d1** are not very stable and some decomposition occurs with time. Fresh solutions of monomer **m1** yield a single-wave cyclic voltammogram characteristic of a diffusion-controlled quasi-reversible monoelectronic transfer (Figure 2A). The standard redox potential of **m1** was determined from the half-wave potential, $E_{1/2} = {}^{1}/_{2}(E_{p,a} + E_{p,c}) = 45$ mV (Figure 2A),

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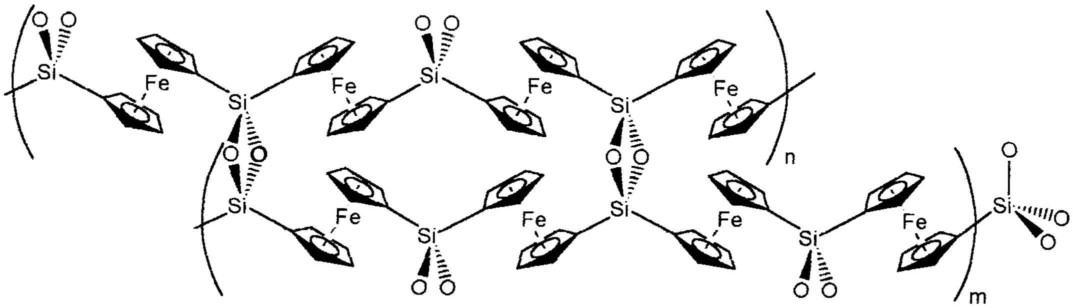

Figure 4. Schematic representation of the idealized structure of **Gp1H**.

relative to the standard redox potential of ferrocene. As expected, monomer **m1** is less easily oxidized than ferrocene as a consequence of the electron-acceptor properties of the two chloride substituents, which decrease the electron density at the iron atom of the oxidized **m1** cation radical. In addition, as in other bridged ferrocenophanes,[31] the deviation and non-coplanarity of the cyclopentadienyl rings in ferrocenediylchlorosilane **m1** are expected to increase $E_{1/2}$.

The cyclic voltammetry of the binuclear complex **d1** exhibits two successive redox systems centered at $(E_{1/2})_1 = 130$ mV and $(E_{1/2})_2 = 480$ mV ($\Delta E_{1/2} = 350$ mV) (Figure 2B). Although the voltamperometric waves are distorted (as a consequence of probable adsorption of decomposition products), the electrode reaction of **d1** appears to involve two consecutive one-electron-oxidation steps to give presumably the corresponding mono- and then diferrocenium cations. This result is similar to that observed with the 1,1,12,12-tetramethyl[1,1]-silaferrocenophane analogue,[27,28] although this last compound is more easily oxidized ($(E_{1/2})_1 = -20$ mV and $(E_{1/2})_2 = 210$ mV) because of the electron-donor properties of the two methyl substituents. The result also shows that it is appreciably more difficult to remove an electron from **d1** than from **m1**, which can be rationalized in terms of the greater electron-attracting effect of the four chloride substituents in **d1**. On the other hand, it is appreciably more difficult to remove from **d1** the second electron than the first, indicating an electronic interaction between the ferrocene and ferrocenium units in the monocationic form of **d1**. This is not surprising, since the Fe···Fe distance in **d1** was found to be only 5.930 Å in the crystal. Thus, strong interactions are expected between the two iron centers, as already observed for compounds such as biferrocenophane ($\Delta E_{1/2} = 630$ mV),[32] a dinuclear [1.1] ferrocenophane with methylene bridges ($\Delta E_{1/2} = 190$ mV)[33] or with dimethylsilyl bridges ($\Delta E_{1/2} = 230$ mV[27] or 250 mV[28]).

The electrochemistry of polymer **p1** was impossible to study, since this compound is an extremely hard, vitreous solid that could not be ground or dissolved. In contrast, the insoluble organic–inorganic material **Gp1H**, obtained by complete hydrolysis of **p1**, can be ground into a powder and immobilized onto an electrode surface as a composite film with poly(tetrafluoroethylene) (PTFE) (see Experimental Section). Cyclic voltammograms (100 mV s^{-1}) of **Gp1H** show two quasi-reversible oxidation waves at $(E_{1/2})_1 = 200$ mV and $(E_{1/2})_2 = 382$ mV ($\Delta E_{1/2} = 182$ mV) (Figure 3). It has been shown that when two ferrocene units in a polymer are joined by a spacer group, two oxidation potentials can result.[16−21] This separation results from interactions between the iron sites and is proportional to the spacer length between the ferrocenyl units. At small separation the interaction is large and yields two distinct oxidation potentials. At large separation, there is no interaction and only a single oxidation potential results.[34] It was thus expected that the **Gp1H** material would exhibit two oxidation potentials, since the synthesis of **Gp1H** should preserve the initial polymer chains, as shown in the simplified representation of Figure 4. In this structure, the polymer chains are linked to each other through Si–C bonds. Since the ferrocenyl units are separated by only one silicon atom, strong interactions are expected, which is confirmed experimentally.

Experimental Section

All reactions were carried out under argon using a vacuum line and Schlenk techniques. Solvents were dried and distilled just before use. Melting points were determined with a Gallenkamp apparatus and are uncorrected. IR data were obtained on a Perkin-Elmer 1600 FTIR spectrophotometer. The ^{1}H and ^{13}C solution NMR spectra were recorded on a Bruker DPX-200 spectrometer, and the ^{29}Si solution NMR spectra were recorded on a Bruker WP-200 SY spectrometer. Solid-state CP MAS NMR spectra were obtained with a Bruker FT AM 300 spectrometer: ^{13}C CP MAS NMR at 75.47 MHz, recycling delay 5 s, and contact time 5 ms; ^{29}Si CP MAS NMR at 59.62 MHz, recycling delay 10 s, and contact time 2 ms. The spinning rate was 5000 Hz in all cases. Chemical shifts are given relative to tetramethylsilane. Specific surface areas were determined using a Micromeritics Gemini III 2375 apparatus. Elemental analyses were carried out by the "Service Central de Micro-Analyse du CNRS".

Reagents, Instrumentation, and Procedure for the Electrochemical Study. Acetonitrile (Rathburn, GPLC grade) was used as received. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka. Poly(tetrafluoroethylene) (PTFE) was purchased from Aldrich. Electrochemical experiments were conducted in a conventional three-electrode cell under an argon atmosphere or in a glovebox (in the case of **m1** and **d1**). The working electrode was either a platinum disk (5 mm) or a vitreous carbon disk (3 mm diameter). Ag/10 mM $AgNO_3$ + 0.1 M TBAP in CH_3CN was used as the reference electrode. The potential of the regular ferrocene/ferrocenium ($Fc/Fc^{\bullet+}$) redox couple, used as an internal standard, was 0.075 V under our experimental conditions. The immobilization of the solid compounds on the electrode surfaces was carried out

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from a colloidal aqueous suspension of 0.3% PTFE using the following procedure: the solid particles of **Gp1H** were first ground in an agate mortar in order to obtain a fine powder; 1 mg of this powder was then mixed in 500 mL of PTFE suspension by ultrasonication; 20 mL of the resulting suspension was spread on the platinum electrode, and the solvent was removed by evaporation at 90 °C during 20 min. At this temperature the PTFE particles are expected to flow on the electrode surface, leading to encapsulation of the solid particles and their immobilization on the surface of the conductive support. This modification of the electrode surface resulted in an adherent thin film which could be studied electrochemically in acetonitrile electrolyte. Electrochemical measurements were carried out using an EG&G PAR Model 273 potentiostat connected to a Sefram TGM 164 X-Y recorder.

Synthesis of p1 and d1. The thermal ring-opening polymerization of **m1**[25,26] was performed according to the procedure described.[26] A Pyrex tube was charged with 2.04 g (7.2 mmol) of **m1** and then sealed under vacuum. The tube was heated at 250 °C for 2 h. A dark red solid deposited in the bottom of the tube, whereas needle-shaped orange crystals formed on the walls of the tube. After it was cooled, the tube was opened in an inert-atmosphere glovebox. Addition of 5 mL of dry THF resulted in the dissolution of the orange crystals, which were separated from the dark red, vitreous, completely THF-insoluble solid **p1** (1.52 g, 5.3 mmol, 73%). The THF solution was concentrated under vacuum and afforded 0.35 g (1.2 mmol, 17%) of dimer **d1**. ^{1}H NMR (CD_2Cl_2) : δ 4.2 (4H, t), 4.7 (4 H, t). ^{13}C NMR (CD_2Cl_2) : δ 70.1 (C-*ipso* on Cp), 73.2, 75.2 (Cp). ^{29}Si NMR (CD_2Cl_2): δ 12.5. Anal. Calcd for $C_{20}H_{16}Cl_4Fe_2Si_2$: C, 42.44; H, 2.85; Cl, 25.05. Found: C, 42.47; H, 2.93; Cl, 24.68.

Crystal Data for d1. A few air-sensitive needles were recovered from the sealed tube and were not recrystallized further. A small plate was mounted in mineral oil and cooled with a stream of nitrogen. The intensities were collected with an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation ($\lambda = 0.710\,69$ Å). The structure was solved by direct methods[35] and difference Fourier syntheses. The hydrogen atoms were positioned by calculation,[36] and their contributions were included in the refinement. Absorption corrections were not performed. Illustrations were performed using the ZORTEP program.[37] Details of data collection and refinement for **d1** are given in Table 1.

Hydrolysis of p1. One gram (3.53 mmol) of polymer **p1** was suspended in 35 mL of THF under an argon atmosphere. A 2.14 g (21.2 mmol) portion of Et_3N and 0.65 g (35.3 mmol) of H_2O were added. The reaction mixture became orange. It was stirred at room temperature for 16 h. The solid was filtered and washed three times with water to remove the ammonium salts. The insoluble solid residue was washed with acetone and diethyl ether, yielding a quantitative amount of an orange, insoluble powder. ^{13}C CPMAS NMR: δ 73. ^{29}Si CPMAS NMR: δ −29. Anal. Calcd for $C_{10}H_8FeOSi$: C, 52.63; H, 3.51; Fe, 24.56; Si, 12.28. Found: C, 51.37; H, 3.89; Fe, 21.60; Si 10.95. No significant specific surface area was found.

Acknowledgment. We thank Prof. R. J. P. Corriu for fruitful discussions and J. Dabosi for her assistance with the experimental work.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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