

Organometallic Silicon Dendrimers

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The first series of organometallic silicon dendritic macromolecules, containing a controlled number of redox-active centres, are synthesized and characterized.

The macromolecules known as dendrimers¹ have attracted great interest. Divergent and convergent step-by-step synthetic approaches have been used and have yielded organic, organosilicon² and a few examples of organometallic³ dendrimers. As a part of our studies of new classes of silicon-containing organometallic compounds,⁴ we now report the synthesis of a novel family of ferrocenyl-containing organosilicon dendrimers which, to our knowledge, represent the first examples of well-characterized organometallic silicon dendritic macromolecules. These compounds show promise for multielectron-transfer redox reactions.

The key chlorosilane dendrimers of this study have been cleanly synthesized starting with tetraallylsilane as the initiator core **G0**, following the valuable divergent approach developed by van der Made and van Leeuwen⁵ (Scheme 1). Thus, Pt-catalysed hydrosilylations of the allyl groups in **G0** with chlorodimethylsilane and dichlorodimethylsilane, afforded **G1Cl** and **G1Cl₂**.[†] Next, growing of the branches in **G1Cl₂** was achieved by allylation of the eight SiCl groups with allylmagnesium bromide, which gave the first generation allyl **G1**. Finally, all the allyl groups in **G1** were hydrosilylated with dimethylchlorosilane, and provided the target dendrimer **G2Cl** with eight reactive SiCl end groups. The structures of the novel silane dendrimers were confirmed by elemental analysis, and by ¹H, ¹³C, and ²⁹Si NMR and IR spectroscopy.

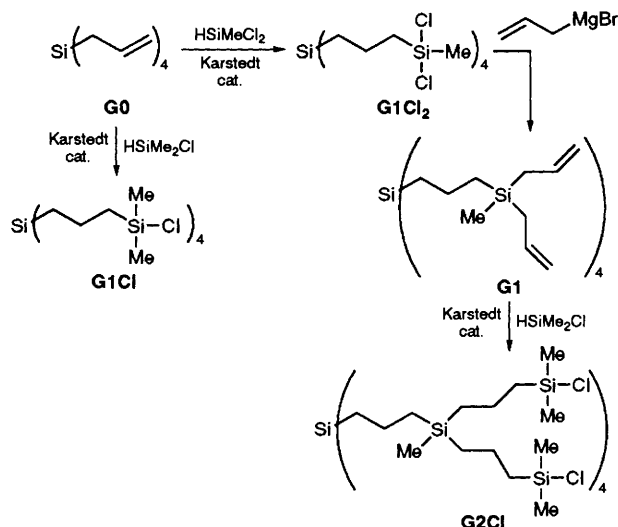
Two different synthetic routes have been used to incorporate ferrocenyl-containing organometallic units into organosilicon dendrimeric polyfunctional cores (Scheme 2). The first, involves treatment of **G1Cl** and **G2Cl** with ferrocenyllithium, in THF at 0 °C.[‡] These reactions afforded the starburst macromolecules **1** and **2**, with four and eight ferrocenyl moieties, respectively. The high reactivity of the Si–Cl bonds towards the amine groups, also allowed another facile organometallic functionalization of the surface of **G1Cl** and **G2Cl**. In this method, we selected β-aminoethylferrocene Fe(η⁵-C₅H₄CH₂CH₂NH₂)(η⁵-C₅H₅), as the starting monomer, because the amino reactive group is two methylene

units removed from the ferrocene nucleus.§ Treatment of **G1Cl** and **G2Cl** with the appropriate mole ratios of β-aminoethylferrocene, in toluene solution, at room temp., and in the presence of Et₃N as the base to neutralize the acidic byproduct liberated in the reaction, provided the expected tetra- and octa-nuclear compounds **3** and **4**. The purification procedures depended on the compound, and generally included hydrolytic workup, sublimation in vacuum of unreacted starting ferrocene or some reaction byproducts, and repeated column chromatographies on silanized silica (eluent hexane or hexane–THF).¶ The novel organometallic compounds **1–4** were isolated as red–orange thick materials, and were structurally characterized by ¹H, ¹³C, and ²⁹Si NMR and IR spectroscopy, elemental analysis and MS.||

The electrochemical properties of **1–4** have been studied. The CVs of each compound exhibited a single reversible oxidation wave.** Evaluation of the number of electrons transferred in the oxidations was effected from the intensity of the CV waves,⁶ and was confirmed by controlled-potential electrolyses. For **1** and **3** the results indicate a four-electron exchange, whereas for **2** and **4** the redox processes correspond to eight-electron oxidations. Differential pulse voltammetry measurements for **1–4** gave only one wave, suggesting that the oxidation of the four (in **1** and **3**), and eight (in **2** and **4**) ferrocenyl moieties occurred at the same potential. Therefore, in these compounds the ferrocenyl moieties are essentially noninteracting redox centres.⁶ In THF solutions, upon oxidation to the polycations, compounds **2** and **4** undergo oxidative precipitation yielding adsorbed films on the Pt electrode surfaces. Thus, modification of electrodes with organometallic dendritic macromolecules will be accessible.

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Scheme 1

Footnotes

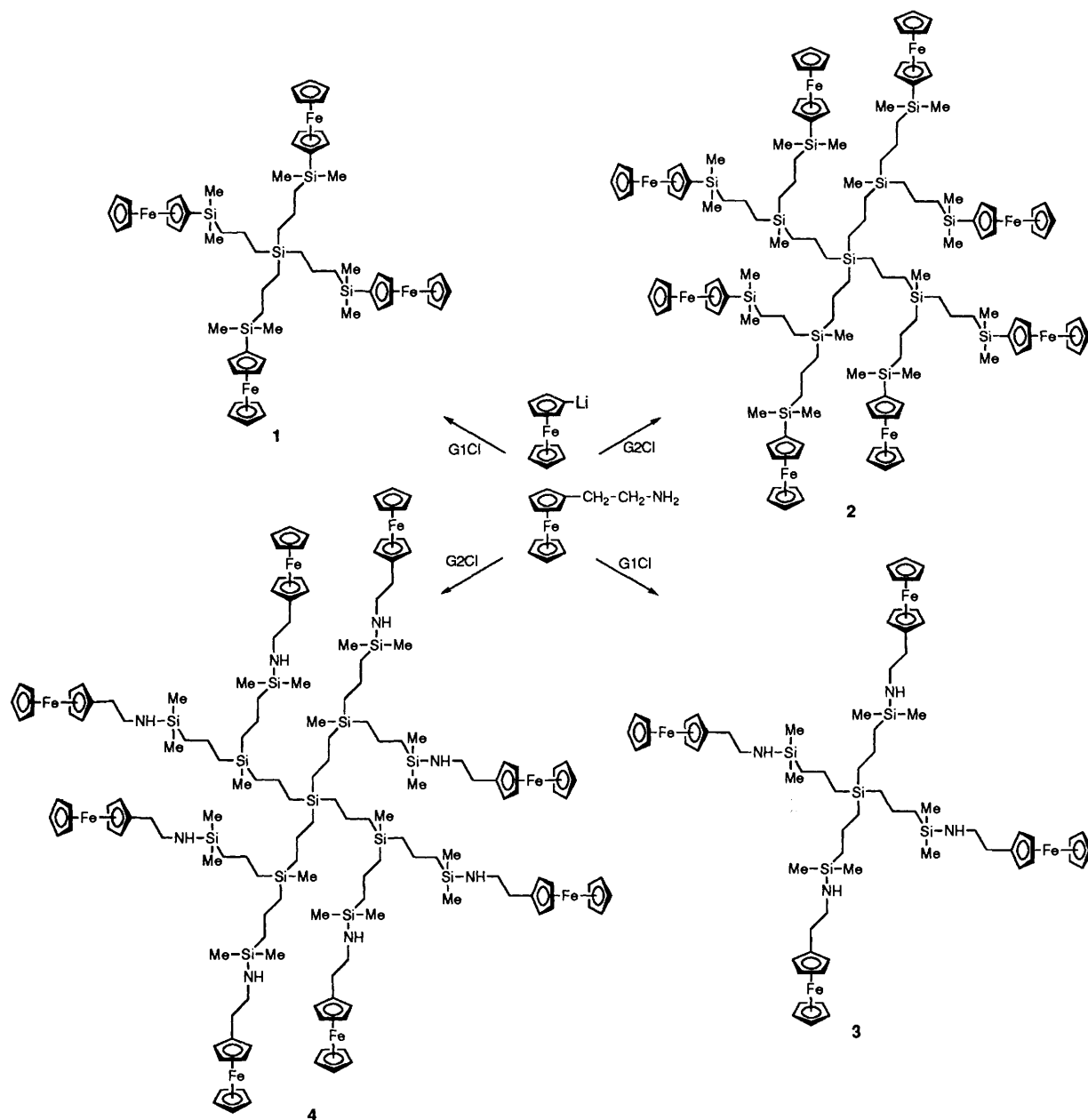
[†] Hydrosilylations have been effected using the Karstedt catalyst [bis(divinyltetramethyldisiloxane)platinum(0) in xylene]. According to the ¹H NMR spectra of the hydrosilylation products, only the β-isomers were formed.

[‡] The monolithiated species Fe(η⁵-C₅H₄Li)(η⁵-C₅H₅) was prepared either by treatment of ferrocene with 0.75 equiv. of *tert*-butyllithium, in THF at 0 °C (see F. Rebiere, O. Samuel and H. B. Kagan *Tetrahedron Lett.*, 1990, **31**, 3121), or by a transmetalation reaction involving the use of (chloromercurio)ferrocene and *n*-butyllithium, in THF at –78 °C (see D. Seyferth, H. P. Hofmann, R. Burton and J. F. Helling, *Inorg. Chem.*, 1962, **1**, 227).

§ This feature minimizes steric and electronic effects due to the organometallic moiety, and the instability found in α-functional ferrocene derivatives, due to the α-ferrocenyl carbonium ion stability is removed. See: K. E. Gonsalves, R. W. Lenz and M. D. Rausch, *Appl. Organomet. Chem.*, 1987, **1**, 81, and references therein.

¶ Experimental procedures, physical properties, and a complete structural characterization of all new compounds described here, will be reported in the full paper.

|| All compounds gave spectroscopic and analytical data in accordance with the assigned structures.



** CV data (vs. SCE), in CH_2Cl_2 with $\text{NBu}_4^+\text{PF}_6^-$. For 1: $E_{1/2} = +0.40$ V. For 2: $E_{1/2} = +0.44$ V. For 3: $E_{1/2} = +0.56$ V. For 4: $E_{1/2} = +0.55$ V.

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- For recent works on dendrimers, also called arborols or cascade molecules, see for example: H. B. Meikelburger, W. Jaworek and F. Vögtle, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1571; D. D. Tomalia, A. M. Naylor and W. A. Goddard, III, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 138; I. Gitsov, K. L. Wooley and J. M. J. Frechet, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1200; G. R. Newkome and C. N. Moorefield, in *Advances in Dendritic Macromolecules*, ed. G. R. Newkome, JAI, Greenwich, CT, 1994.
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