

Preliminary communication

Silicon-based organometallic dendritic macromolecules containing
 $\{\eta^6\text{-}(\text{organosilyl})\text{arene}\}$ chromium tricarbonyl moieties

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Abstract

Novel organosilicon dendrimers peripherally functionalized with aromatic rings, $\text{Si}[(\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{C}_6\text{H}_5]_4$ (**G1Ph**₁) and $\text{Si}[(\text{CH}_2)_3\text{Si}(\text{CH}_3)((\text{CH}_2)_3\text{Si}(\text{CH}_3)_2\text{C}_6\text{H}_5)_2]_4$ (**G2Ph**₁), have been constructed employing a divergent synthetic approach. The π -coordinating ability of these surface located arene rings towards transition metals has allowed the synthesis of a new family of organometallic dendritic macromolecules 1–3, containing η^6 -coordinated $\text{Cr}(\text{CO})_3$ moieties at the periphery of organosilicon dendritic cores.

Keywords: Chromium; Silicon; Organometallic dendrimers

The design, synthesis and characterization of highly branched dendritic macromolecules, is an area of research which is undergoing dramatic growth [1]. The incorporation of organometallic moieties into dendritic structures [2,3], represents a challenge of growing interest since it provides new valuable opportunities to modify the unusual properties of dendrimers, as well as for tailoring a rich variety of nanostructured organometallic macromolecules of desired nuclearity, possessing new topologies, and exhibiting attractive electrical, optical, magnetic and catalytic properties. Remarkably, dendritic macromolecules containing a controlled number of redox-active organometallic centers are good candidates to play a key role in a number of applications such as in multi-electron redox catalysis, photoinduced electron-transfers, and molecular electronic devices.

As part of our ongoing studies on silicon-containing organometallic compounds [4], we recently synthesized a new class of ferrocenyl silicon dendrimers [5], and we have demonstrated the feasibility of modifying electrode surfaces with these redox active organometallic dendritic macromolecules [6]. In our quest of new approaches to the organometallic modification of den-

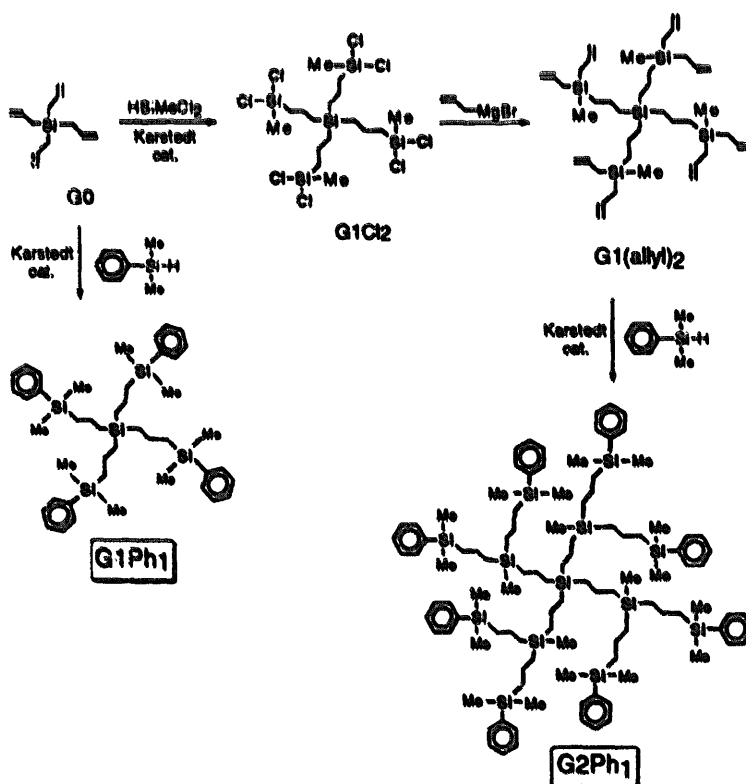
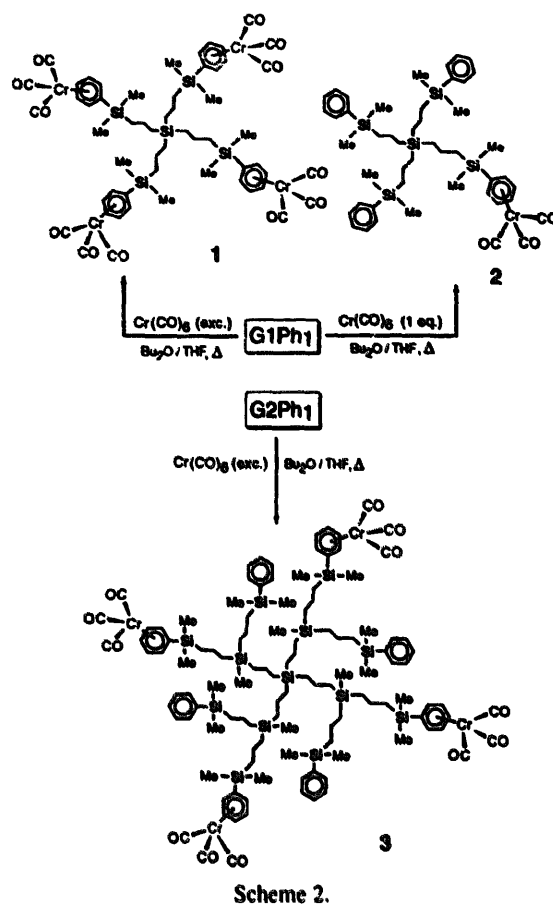
drimers, we have now explored pathways that allow the efficient π -coordination of transition metals to terminal arene ligands on organosilicon dendrimers. Thus, we report here our preliminary results on the synthesis and characterization of a novel family of silicon-based dendritic structures, in which peripheral aromatic rings are π -complexed to chromium tricarbonyl moieties.

The key silicon-based dendrimers functionalized at the periphery with aromatic rings, required for this study were **G1Ph**₁ and **G2Ph**₁, which were prepared following a divergent approach which starts with tetraallylsilane (**G0**) as four-directional, tetrahedral center of branching [7] (see Scheme 1). The procedure follows approximately the valuable methodology developed by Seyferth et al. [8], Zhou and Roovers [9] and van der Made and van Leeuwen [10], for the synthesis of organosilicon dendrimers, and involves hydrosilylations (with $\text{C}_6\text{H}_5\text{SiMe}_2\text{H}$ as terminal unit, and/or Cl_2SiMeH as two-directional branching unit), and allylation (with $\text{MgBrCH}_2\text{CH}=\text{CH}_2$) as the growing steps. The structures of the novel phenyl functionalized dendrimers were confirmed by elemental analysis, and by ¹H, ¹³C, and ²⁹Si NMR and IR spectroscopy. The ¹H NMR spectra for **G1Ph**₁ and **G2Ph**₁ showed in both cases the resonances for the methyl and methylene protons with chemical shifts in the corresponding regions of the

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spectrum, together with the characteristic resonances of the phenyl rings, in the expected integrated ratio (see for example Fig. 1A). The ^{29}Si NMR spectra display clearly separated signals for the different types of silicon atoms in the molecules, which can be easily assigned on the basis of the chemical shifts and the peak intensities. Thus, the outermost silicon atoms attached to the phenyl rings resonate at -3.52 (for G1Ph_1) and -3.72 ppm (for G2Ph_1) upfield of the central Si atoms, and also of the third different silicon atom in G2Ph_1 , which appear near 1.2 ppm.

Our first synthetic approach for incorporating $\text{Cr}(\text{CO})_3$ moieties into organosilicon dendritic cores involved thermal replacement of CO from chromium hexacarbonyl by the phenyl-terminated G1Ph_1 and G2Ph_1 (Scheme 2). Thus, treatment of G1Ph_1 with an excess of $\text{Cr}(\text{CO})_3$ in $\text{Bu}_2\text{O}/\text{THF}$ (9/1) at 140°C , affords the tetranuclear dendrimer **1**, which was isolated as moderately air-stable yellow crystals [11]. Similarly, by using 1 equiv. of $\text{Cr}(\text{CO})_3$, the mononuclear macromolecule **2** was also prepared. This thermal synthetic procedure has also been attempted to obtain the next higher generation, but the complete functionalization of the eight phenyl-terminated dendrimer arms of G2Ph_1 with $\text{Cr}(\text{CO})_3$ units did not succeed. Instead, from the reaction of $\text{Cr}(\text{CO})_3$ with G2Ph_1 , the tetranuclear dendrimer **3** was isolated as the major reaction product [12]. The failure in obtaining the octachromium macro-



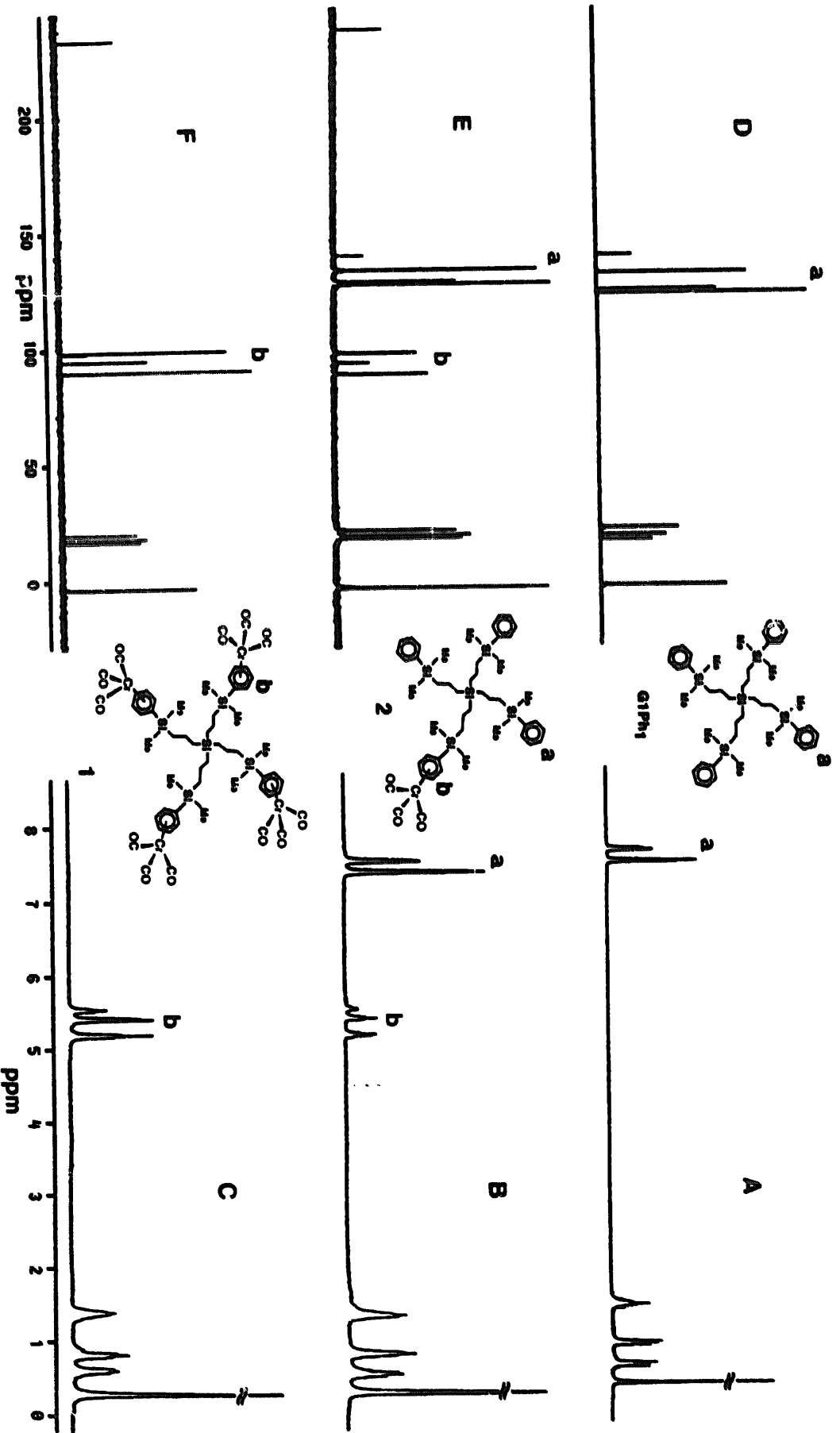


Fig. 1. ^1H NMR (300 MHz, CDCl_3) (A-C) and ^{13}C (^1H) NMR (75.43 MHz, CDCl_3) (D-F) spectra of dendrimers G1Ph₁, 1 and 2.

molecule was presumably caused by the more forcing reaction conditions (considerably longer reaction periods with elevated temperatures) required for the incorporation of high loadings of $\text{Cr}(\text{CO})_3$ units from $\text{Cr}(\text{CO})_6$, which can produce noticeable decomposition. In order to obtain the desired macromolecule with eight η^6 -coordinated $\text{Cr}(\text{CO})_3$ moieties, and on the basis of our previous experiences, work is currently in progress aimed to overcome these problems by reacting reactive derivatives such as $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ and $(\eta^6\text{-C}_6\text{H}_5\text{Li})\text{Cr}(\text{CO})_3$, or even better $(\eta^6\text{-C}_6\text{H}_5\text{SiMe}_2\text{H})\text{Cr}(\text{CO})_3$, and $(\eta^6\text{-C}_6\text{H}_5\text{SiMe}_2\text{CH}=\text{CH}_2)\text{Cr}(\text{CO})_3$ [13], with the appropriate dendrimers with terminal Si-Ph, Si-Cl, Si-allyl and Si-H functional groups, under milder reaction conditions.

The structures of the novel organometallic dendrimers 1–3 were straightforwardly established on the basis of elemental analysis, IR and multinuclear (^1H , ^{13}C , ^{29}Si) NMR spectroscopy and mass spectrometry. Evidence for the η^6 -coordination of the $\text{Cr}(\text{CO})_3$ moieties included the presence of the two typical $\nu(\text{C}\equiv\text{O})$ strong bands near 1970 and 1880 cm^{-1} in the IR spectra, and resonances at ca. δ 233 ppm due to the carbonyl carbon atoms in the ^{13}C NMR spectra (see Fig. 1E and 1F). Specifically, in the ^1H NMR spectrum of 1 (Fig. 1C) the complete η^6 -coordination of the $\text{Cr}(\text{CO})_3$ moieties to the four phenyl rings in the dendritic silicon core was confirmed by the total absence of resonances in the range 7.37–7.55 ppm, in which the arene ligand resonances of the noncoordinated organosilicon dendrimer are observed (see Fig. 1A). As a consequence of the withdrawal of the π -electrons from the arene rings by the $\text{Cr}(\text{CO})_3$ moieties, the aromatic protons on the complexed dendrimer resonate at a significantly higher field, in the region from 5.6 to 5.1 ppm. The symmetric structure of 1 was also unequivocally confirmed by the ^{13}C NMR spectrum (Fig. 1F), which displays exclusively the resonances expected for the different carbon atoms, with the characteristic upfield shifts of ca. 30 ppm in the resonances of the coordinated arene carbon nuclei relative to the uncoordinated aromatics in dendrimer **G1Ph**₁ (Fig. 1D). Likewise, the ^1H NMR spectra of 2 (Fig. 1B) and 3 have been particularly useful to verify the loading of $\text{Cr}(\text{CO})_3$ units on the dendrimers. Thus, the integration ratio of the protons in the complexed arene ring and those of the uncomplexed aryl moieties in both organometallic dendrimers are in agreement with the proposed mono and tetrametallic structures. The FAB mass spectrum of 1 shows peaks which term from species formed by successive loss of carbon monoxide ligands and $\text{Cr}(\text{CO})_3$ moieties.

Attempts to isolate dendrimers 1 and 3 in a crystalline form suitable for X-ray structural determination have so far been unsuccessful. Nevertheless, using computer-generated molecular (CACHTM) we have measured approximate diameters of 2 and 3 nm for these

first and second generation organometallic dendrimers, respectively.

The electrochemical behavior of the tetra- and mononuclear dendrimers 1 and 2 was studied by cyclic voltammetry and differential pulse voltammetry, in a nonnucleophilic medium, $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{NPF}_6$ [14]. Both dendrimers exhibit a first chemically reversible oxidation wave ($E_{1/2} = +0.78$ and $+0.80 \text{ mV}$ vs. SCE, respectively), which formally corresponds to the oxidation of the zero valent chromium centers to the chromium(I) oxidation state in the peripheral ($\eta^6\text{-C}_6\text{H}_5$) $\text{Cr}(\text{CO})_3$ units. Evaluation of the number of electrons transferred in the processes was effected from the intensity of the cyclic voltammetric waves [15], which indicates that for dendrimer 1, the oxidation wave corresponds to the transfer of four electrons, at the same potential, resulting the cationic dendritic species [1^{4+}] which is stable in the cyclic voltammetric time scale. Likewise, in the tetrametallic 1, the tricarbonylchromium moieties are essentially noninteracting redox centers. At more positive potentials a second irreversible process is also observed. Furthermore, when the oxidation was effected in the presence of tertiary phosphite nucleophiles, the cationic species [1^{4+}] undergoes rapid CO substitution, which has also been studied by spectroelectrochemical (IR and EPR) techniques.

Remarkably, we anticipate that the ability for transition metal π -complexation exhibited by the peripheral aromatic rings of the novel silicon-based dendrimers **G1Ph**₁ and **G2Ph**₂ should have a large scope, since it provides an enhanced variability for the designed construction of novel families of dendritic macromolecules with different organotransition metal moieties.

Acknowledgements

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References and notes

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- [7] **G1Ph₁**: A toluene solution (50 ml) of **G0** (1.60 g, 8.33 mmol), 10 μ l of a solution of Karstedt's catalyst (3%–5% Pt in xylene), and phenyldimethylsilane (5 g, 36.70 mmol) was stirred for 24 h at room temperature. After the complete disappearance of the allyl protons (confirmed by IR and ¹H NMR), the excess of C₆H₅SiMe₂H was removed under vacuum, and the residue was redissolved in hexane and filtered through silanized silica. The solvent was removed to afford **G1Ph₁** as a pure colorless viscous oil. Yield: 5.69 g (96%). ¹H NMR (CDCl₃): δ 0.31 (s, 24H, SiCH₃), 0.55 (t, 8H, CH₂Si), 0.84 (t, 8H, CH₂SiPh), 1.37 (m, 8H, CH₂CH₂CH₂), 7.40 (m, 12H, C₆H₅), 7.55 (m, 8H, C₆H₅). ¹³C{¹H}NMR (CDCl₃): δ -2.79 (CH₃), 17.45 (SiCH₂), 18.60 (CH₂SiPh), 20.62 (CH₂CH₂CH₂), 127.77, 128.79, 133.58, 139.82 (C₆H₅). ²⁹Si{¹H}NMR (59.3 MHz, CDCl₃): δ -3.52 (SiPh), 1.16 (SiCH₂). Anal. Calc. for Si₅C₄₄H₆₈: C, 71.70; H, 9.31. Found: C, 71.89; H, 9.20.
- G2Ph₁** was prepared analogously to **G1Ph₁**, starting from 1.50 g (2.15 mmol) of **G1(allyl)₂**, and 2.72 g (20 mmol) of C₆H₅SiMe₂H. After chromatographic purification with hexane as eluent **G2Ph₁** was isolated as a colorless viscous oil. Yield: 1.91 g (50%). ¹H NMR (CDCl₃): δ 0.07 (s, 12H, SiCH₃), 0.29 (s, 48H, CH₃SiPh), 0.58 (m, 32H, CH₂SiCH₂), 0.84 (m, 16H, CH₂SiPh), 1.37 (m, 24H, CH₂CH₂CH₂), 7.37 (m, 24H, C₆H₅), 7.53 (m, 16H, C₆H₅). ¹³C{¹H}NMR (CDCl₃): δ -4.95 (SiCH₃), -2.85 (CH₃SiPh), 18.47, 18.59, 18.70, 20.42 (CH₂), 127.6, 128.7, 133.9, 139.7 (C₆H₅). ²⁹Si{¹H}NMR (CDCl₃): δ -3.72 (SiPh), 1.17 (SiCH₃), 1.27 (SiCH₂). Anal. Calc. for Si₁₃C₁₀₄H₁₇₂: C, 69.91; H, 9.71. Found: C, 69.67; H, 9.59. Detailed synthetic procedures and key data for the intermediate dendrimers **G1Cl₂** and **G1(allyl)₂** will be reported in the full paper.
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- [10] A.W. van der Made and P.W.N.M. van Leeuwen, *J. Chem. Soc., Chem. Commun.*, (1992) 1400.
- [11] **1**: A solution of **G1Ph₁** (1.00 g, 1.36 mmol) and Cr(CO)₆ (2.40 g, 10.9 mmol) in Bu₂O/THF (90/10 ml) were heated at reflux for 72 h. The progress of the reaction was monitored by IR and ¹H NMR spectroscopies. The suspension was filtered through silanized silica to remove insoluble decomposition products and some unreacted Cr(CO)₆. From the resulting solution the solvent was removed in vacuum together with any remaining Cr(CO)₆ affording an oil, which after standing at -30°C in hexane solution gives **1** as a yellow solid. Yield: 65% (1.14 g). The solid can be further purified by recrystallization from hexane/CH₂Cl₂ to yield **1** as yellow crystals. ¹H NMR (CDCl₃): δ 0.27 (s, 24H, SiCH₃), 0.59 (t, 8H, CH₂Si), 0.81 (t, 8H, CH₂SiPh), 1.38 (m, 8H, CH₂CH₂CH₂), 5.17, 5.38, 5.52 (m, 20 H, C₆H₅Cr(CO)₃). ¹³C{¹H}NMR (CDCl₃): δ -3.05 (CH₃), 17.24 (SiCH₂), 18.45 (CH₂SiPh), 20.29 (CH₂CH₂CH₂), 90.61, 95.38, 99.09, 99.39, (C₆H₅Cr(CO)₃), 233.14 (CO). IR (CH₂Cl₂) ν (C=O) 1966 and 1888 cm⁻¹. MS (FAB: *m/z* (%)): 1198 (M⁺ - 3CO, 10.0), 1061 (M⁺ - [Cr(CO)₃] - 3CO, 32.4), 925 (M⁺ - 2[Cr(CO)₃] - 3CO, 31.5), 841 (M⁺ - 2[Cr(CO)₃] - 6CO, 12.0), 789 (M⁺ - 3[Cr(CO)₃] - 3CO, 100). Anal. Calc. for Si₆C₅₆H₆₈Cr₆O₁₂: C, 52.50; H, 5.35. Found: C, 51.99; H, 5.39. **2**: This dendrimer was prepared analogously to **1**, starting from 1.00 g (1.36 mmol) of **G1Ph₁** and 0.30 g, (1.36 mmol) of Cr(CO)₆. After filtration of the reaction mixture and removal of the solvent, the product was subjected to repeated chromatographic purifications over silanized silica with hexane as eluent, to afford **2** as a yellow viscous oil. Yield: 0.35 g (31%). ¹H NMR (CDCl₃): δ 0.23 (s, 24H, SiCH₃), 0.49 (m, 8H, CH₂Si), 0.76 (m, 8H, CH₂SiPh), 1.29 (m, 8H, CH₂CH₂CH₂), 5.13, 5.35 and 5.47 (m, 5H, C₆H₅Cr(CO)₃), 7.34 and 7.84 (m, 15H, C₆H₅). ¹³C{¹H}NMR (CDCl₃): δ -2.64 (CH₃SiPh), -2.94 (CH₃SiC₆H₅Cr(CO)₃), 17.51 (SiCH₂), 18.71 (CH₂SiPh), 20.58 and 20.72 (CH₂CH₂CH₂), 95.41, 99.31, 99.51, 99.73 (C₆H₅Cr(CO)₃), 127.9, 128.9, 133.6, 139.7 (C₆H₅), 233.14 (CO). IR (CH₂Cl₂) ν (C=O) 1965 and 1885 cm⁻¹. Anal. Calc. for Si₅C₄₇H₆₈Cr₁O₅: C, 64.65; H, 7.86. Found: C, 64.49; H, 7.79.
- [12] **3**: This dendrimer was obtained by the same thermal procedure as that described for **1**, starting from 0.55 g (0.30 mmol) of **G2Ph₁**, and Cr(CO)₆ 1.20 g (5.30 mmol). After purification of the reaction mixture as above, the residue was subjected to repeated chromatographic purifications over silanized silica with a mixture of hexane/CH₂Cl₂ as eluent, to afford a major product **3** as an oil, which after standing at -30°C gives a yellow glassy solid. Several fractions of the chromatographic separation also afforded other partially functionalized dendrimers as single species, but in negligible yields. Yield of **3**: 30% (0.18 g). ¹H NMR (CDCl₃): δ -0.13 (s, 12H, SiCH₃), 0.24 (s, 48H, CH₃SiPh), 0.52 (m, 32H, CH₂SiCH₂), 0.79 (m, 16H, CH₂SiPh), 1.33 (m, 24H, CH₂CH₂CH₂) 5.12, 5.36 and 5.46 (m, 20H, C₆H₅Cr(CO)₃), 7.33 (m, 12H, C₆H₅), 7.49 (m, 8H, C₆H₅). ¹³C{¹H}NMR (CDCl₃): δ -4.87 (SiCH₃), -2.78 (CH₃SiPh), -2.48 (CH₃SiC₆H₅Cr(CO)₃), 17.78, 18.71, 20.45 (CH₂), 90.55, 95.25, 99.32 (C₆H₅Cr(CO)₃), 127.7, 128.7, 133.6, 139.8 (C₆H₅), 233.1 (CO). IR (CH₂Cl₂) ν (C=O) 1969 and 1895 cm⁻¹. Anal. Calc. for Si₁₃C₁₁₆H₁₇₂Cr₄O₁₂: C, 59.77; H, 7.44. Found: C, 59.53; H, 7.39.
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