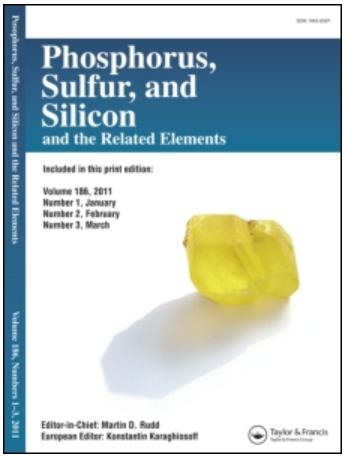

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Novel Carbosiloxane Dendrimers with End-Grafted Highly Functionalized Building Blocks

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This article concentrates on the divergent growth method for the preparation of $SiOCH_2CH_2CH_2$-based carbosiloxane dendrimers by applying repetitive hydrosilylation-alcoholysis cycles. The silicon atoms thereby act as the branching points producing a tetrahedral four directional core as well as 1→1 and 1→2 branching centres.

Keywords: Carbosiloxane; Dendrimers; Hydrosilylation; Alcoholysis

INTRODUCTION

Since the early work of Vögtle and Newkome main-group element and transition metal based dendrimers have gained considerable interest in macromolecular chemistry, due to their highly branched molecular structure as well as their specific chemical and physical properties.[1,2,3,4,5]

Among them, *e.g.* carbosilane dendrimers can be prepared by repetitive hydrosilylation-alkylation cycles in high yield.[6] One characteristic feature of these mono disperse molecules, which possess a regular as well as a highly-branched three-dimensional architecture, is their lipophilic character, which can be explained by the nature of the

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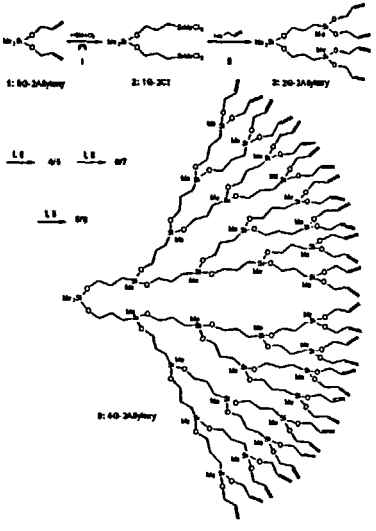
silicon-carbon bonds. However, there is only little known about regular carbosiloxane dendrimers featuring alternating Si-O-C units.[7,8,9]

We here describe an efficient hydrosilylation-alcoholysis route for the preparation of carbosiloxane dendrimers as well as their surface modification with organic, inorganic or even organometallic building blocks.

RESULTS AND DISCUSSION

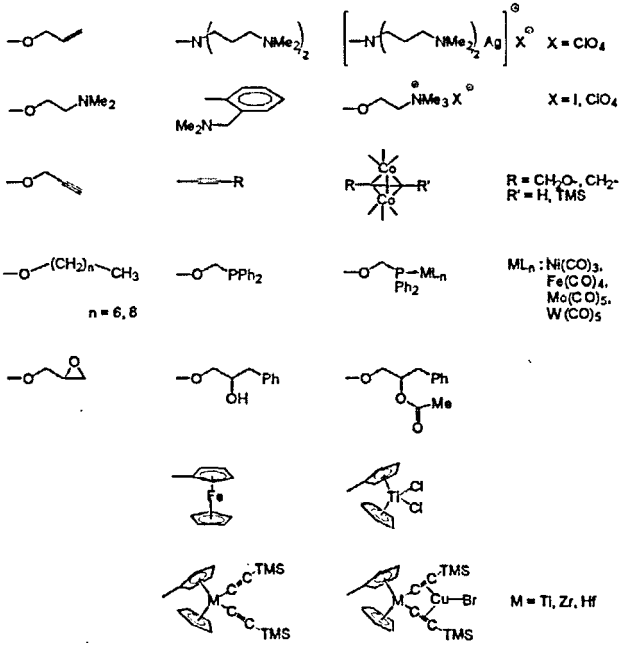
Carbosiloxane dendrimers in which the dendritic scaffold contains alternating $SiOCH_2CH_2CH_2$ units can be synthesised by the divergent growth method by starting with $Si(OCH_2CH{=}CH_2)_4$[10], $MeSi(OCH_2CH{=}CH_2)_3$[11] or $Me_2Si(OCH_2\text{-}CH{=}CH_2)_2$[11] as core molecules.



SCHEME 1 Repetitive synthetic cycles for the preparation of **9** (nG-Cl = n^{th} generation of the appropriate chloro-substituted dendrimer; nG-Allyloxy = n^{th} generation of the appropriate allyloxy dendrimer; n = 1 – 4).[11]

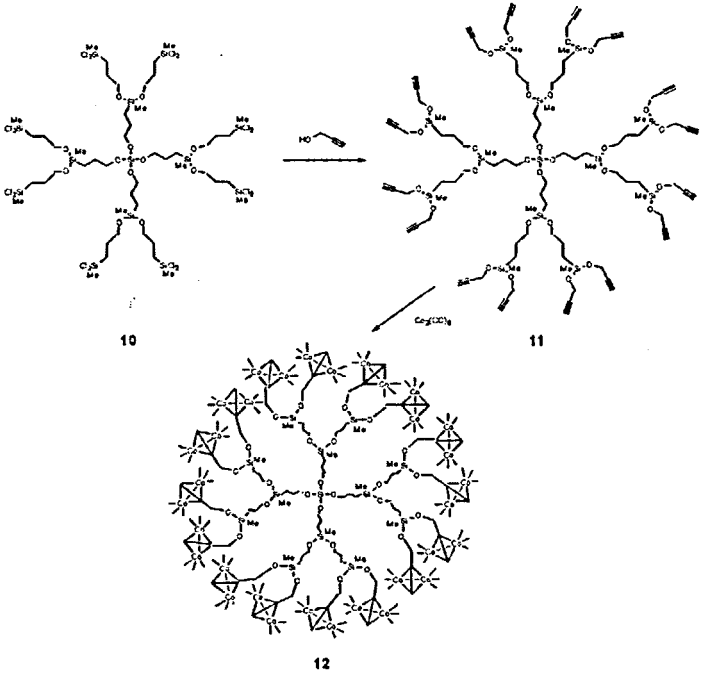
Repetitive reaction sequences with *e.g.* H-$SiMeCl_2$ (hydrosilylation step) and $HOCH_2CH{=}CH_2$ (alcoholysis step) produce the appropriate dendrimers in excellent to quantitative yields. For the so far synthesised carbosiloxane dendrimers the example of the 2-dimensional view of the 4th generation carbosiloxane dendrimer **9** is shown in Scheme 1.[11]

The dendritic species described above contain as end-grafted groups $SiMe(OCH_2CH{=}CH)_2$ or $SiMeCl_2$ entities, which allow the introduction of a wide variety of different main-group element and transition metal fragments. A selection thereof is presented below. [12,13,14,15, 16,17,18,19]



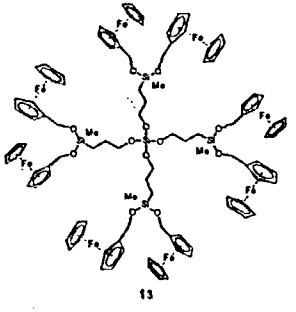
The end-grafted building blocks shown above can successfully be introduced on the dendritic surface by using hydrosilylation, alkylation, alcoholysis or aminolysis steps. Exemplary, the construction of the 2nd generation dendrimer **12** is illustrated in Scheme 2. The synthesis of **12**

involves the reaction of the SiCl-containing dendrimer **10** with $HOCH_2C{\equiv}CH$ and complexation of the C≡C triple bond by $Co_2(CO)_6$, in-situ generated from $Co_2(CO)_8$.[19]



SCHEME 2 Synthesis of dendrimer **12**.[19]

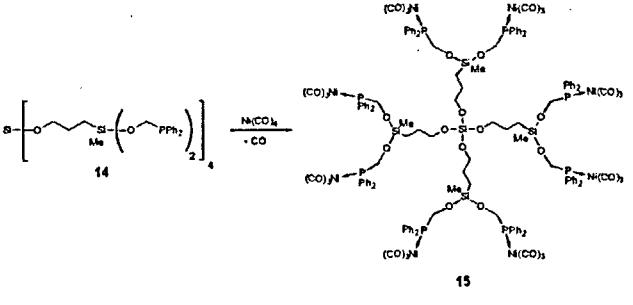
Furthermore, end-grafted $OCH_2[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$ units can be introduced at the dendrimer surface by reacting $SiMeCl_2$-terminated species with $HOCH_2[(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$ in presence of NEt_3 as base (Figure 1).[20]



13

FIGURE 4 2-dimensional view of **13**.[20]

Alcoholysis also plays an important role in the synthesis of cascade molecules containing terminal $-SiOCH_2PPh_2 \rightarrow ML_n$ [ML_n = $Ni(CO)_3$, $Fe(CO)_4$] organometallic entities. The metal carbonyl building blocks ML_n can be introduced *via* $Ph_2PCH_2OSiMe_2$-end-grafted moieties, which themselves are formed by alcoholysis of Si-Cl bonds with $HOCH_2PPh_2$.[13,16] Thus, subsequent reaction of *e.g.* $Si(OCH_2CH_2CH_2\text{-}SiMe(OCH_2PPh_2)_2)_4$ (**14**) with $Ni(CO)_4$ or $Fe_2(CO)_9$ results in the formation of the corresponding $SiOCH_2PPh_2 \rightarrow ML_n$-end-grafted systems **15** [ML_n = $Ni(CO)_3$] and **16** [ML_n = $Fe(CO)_4$] (Figure 2).[13,16]



14 15

FIGURE 2 Preparation of the dendritic molecule **15**.[13,16]

The above described carbosiloxane dendrimers were fully characterised by elemental analysis, MALDI-TOF or ESI-APCI-TOF mass spectrometry, GPC as well as IR and NMR (^1H, $^{13}C\{^1H\}$,

$^{29}Si\{^1H\}$, $^{31}P\{^1H\}$) spectroscopy. The latter two techniques are particularly useful tools to demonstrate that the prepared dendritic $SiOCH_2CH_2CH_2$-based molecules are uniform and that the $SiOCH_2CH{=}CH_2$-, $SiOCH_2{\equiv}CH$-, $SiMeCl_2$- or $SiMeCl_2$-functionalized cascade systems have been completely transformed into the corresponding organic or organometallic modified species.[11]

Acknowledgements
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