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FUNCTIONALIZATION OF CARBOSILANE DENDRIMERS WITH CYCLOPENTADIENYL TITANIUM(IV) COMPLEXES

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Recently, we focused our interest on the synthesis of carbosilane dendrimers with cyclopentadienyl titanium compounds on their periphery. The first strategy consisted in binding monocyclopentadienyl titanium complexes via a Ti-O bond. Dendritic polyols of the second and third generation 2G-OH_8, 2G-OH_{16}, and 3G-OH_{16} were prepared by hydroboration/oxidation of allyl terminated carbosilane dendrimers and used as supports for immobilization of cyclopentadienyltrichlorotitanium(IV) complexes via alcoholysis. Their reaction with $CpTiCl_3$ gave metallodendrimers 2G-$(OTiCpCl_2)_8$, 2G-$(OTiCpCl_2)_{16}$, and 3G-$(OTiCpCl_2)_{16}$, respectively, whereas the reaction of the dendrimers with $CpSi^FTiCl_3$ ($CpSi^F$ = $C_5H_4SiMe_2CH_2CH_2C_8F_{17}$) [1,2] yielded peripherally fluorinated metallodendrimers 2G-$(OTiCpSi^FCl_2)_8$ and 3G-$(OTiCpSi^FCl_2)_{16}$. The resulting materials, however, showed low solubility and stability [3].

Therefore we turned our attention towards binding dicyclopentadienyl titanium(IV) complexes via a Cp ring. Similar materials were reported by Seyferth *et al* in patent literature but their proper characterization has never been published. First and second generation dendrimers with vinyls on their periphery (1G-vin_4, 1G-vin_8, 2G-vin_8, 2G-vin_{16}) were prepared. Three substituted cyclopentadienes with a variable length of spacer between Si-H moiety and cyclopentadiene ring were synthesized. Unsymmetrically substituted titanocene dichlorides bearing those ligands and unsubstituted cuclopentadienyls were then obtained after deprotonation and reaction with $CpTiCl_3$. In the capping reaction, metallodendrimers were constructed by anchoring the titanium dichlorides to the periphery of vinylated carbosilane dendrimers by hydrosilylation [4]. This process was optimized, three parameters: dendrimer generation, branching degree at the periphery and thus the functionalization density and finally the length of the alkylidene spacer were varied systematically resulting in the series of 11 functionalized, metal-decorated macromolecules.

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