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Organic Chemistry, Polymers – I

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O-074

CYCLOPENTADIENYL TITANIUM(IV) COMPLEXES WITH FLUOROUS PONYTAILS IMMOBILIZED ON CARBOSILANE DENDRIMERS VIA A TI-O BOND

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Recently we synthesized light^[1] and heavy^[2] fluoruous cyclopentadienes with silyl substituents bearing up to three fluoruous ponytails. Both monocyclopentadienyltrichlorotitanium and dicyclopentadienyldichlorotitanium (titanocene) complexes were prepared starting from the new ligands. We wondered, whether the monocyclopentadienyl complexes could be immobilized on a soluble polymeric support with low polydispersity, i.e. a carbosilane dendrimer. To provide comparison, reactions with nonfluorinated complexes were also carried out.

Dendritic polyols of the second and third generation 2G-OH₈, 2G-OH₁₆, and 3G-OH₁₆ 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 CpTiCl₃ gave metallodendrimers

2G-(OTiCpCl₂)₈, 2G-(OTiCpCl₂)₁₆, and 3G-(OTiCpCl₂)₁₆, respectively, whereas the reaction of the dendrimers with

CpSi^FTiCl₃ (CpSi^F = C₅H₄SiMe₂CH₂CH₂C₈F₁₇) yielded peripherally fluorinated metallodendrimers 2G-(OTiCpSi^FCl₂)₈ and

3G-(OTiCpSi^FCl₂)₁₆. All metallodendrimers were characterized by multinuclear NMR spectroscopy and the proposed structure was further confirmed by comparison with model 1-propoxycomplexes.^[3]

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Organometallic Chemistry, catalysis, new frontiers – I

O-075

BIDENTATE LEWIS ACID CATALYSIS – A NEW ENTRY TO HIGHLY SUBSTITUTED NAPHTHALENES

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Multidentate interactions are the secret to nature's catalysis. Nonetheless, the application of these principles remains an extremely challenging endeavor. In organic synthesis the Lewis acid catalysis presents a very effective tool for a variety of different transformations. Although effort has been made towards bidentate Lewis catalysts still they react in a monodentate fashion.^[1]

Recently, we were able to show the catalysis of the inverse electron-demand Diels-Alder (IEDDA) reaction of 1,2-diazines by a bidentate Lewis acid in a bidentate fashion.^[2] The general principle is based on the following rationale: The twofold coordination of the bidentate Lewis acid to the 1,2-diazine decreases the energy level of the LUMO facilitating the cycloaddition step. Consecutive elimination of N₂ generates the product and also liberates the catalyst.

This new concept of catalysis is furthermore combined with a novel one-pot synthesis of 1,2-diazino aromatics, developed in our group, to produce highly substituted naphthalenes in two steps from aromatic aldehydes. This strategy was applied for an efficient preparation of Naproxen.

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