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Review

Phosphorus dendrimers as supports of transition metal catalysts

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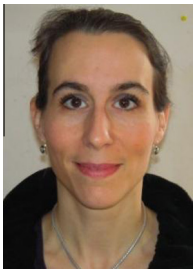
ABSTRACT

Dendrimer are hyperbranched macromolecules, which can be used as support of catalytic entities. This review focusses on polyphosphorhydrazone (PPH) dendrimers, bearing as terminal groups, transition metal complexes of 3d elements (Cu, Sc) and 4d elements (Pd, Ru, Rh). These complexes have been used as catalysts for various organic reactions, in particular C–C couplings. Most of these dendritic complexes can be recovered and re-used several times (up to 12 successive runs with the same efficiency). In several cases, a dendritic (or dendrimer) effect is observed, i.e., an increased efficiency and/or enantioselectivity when comparing a monomeric catalyst with increasing generations of the dendrimers, using in all cases the same number of catalytic entities.

Anne-Marie Caminade *is Director of Researches at the CNRS in Toulouse since 1997 (first class since 2004) and presently head of the "Dendrimers and Heterochemistry" group at the LCC Toulouse since 2006. After two PhDs from the University of Toulouse (1984 and 1988) and two Post-docs (IFP-Paris and Von Humboldt fellow in Saarbrücken), she was recruited at the CNRS in 1985. She developed several aspects of phosphorus chemistry, including low coordinated compounds, transition metals coordination, and macrocycles syntheses. Her current research interest is on the synthesis, reactivity, and applications of dendrimers in particular as catalysts, for nanomaterials and for biology. She is the co-author of more than 390 publications in journals, 40 book chapters and 30 patents (h index 56).*



Armelle Ouali *received her PhD from the University of Montpellier in 2005 in the field of copper-catalyzed arylation of nucleophiles (Dr Marc Taillefer). After a post-doc in the synthesis of phosphorous and silicon-based dendrimers for biological applications (Drs Jean-Pierre Majoral and Anne-Marie Caminade, Toulouse), she moved to the University of California for a post-doc in carbene chemistry (Prof. Guy Bertrand, Riverside). She joined the group of Dr Anne-Marie Caminade in 2008 where she is involved in the development of new catalytic systems for various applications in organic synthesis. Her current interest is the design of dendrimeric metal-based or organic catalysts.*

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Régis Laurent *was born in Porvoo (Finland) and studied chemistry at the University of Toulouse (France) where he received his PhD in 1994 under the supervision of Pr. J. Dubac and Pr A. Laporterie, working on microwave activation in organic chemistry. After post-doctoral studies for the BASF Company at the University of Saarbrücken (Germany) in the group of M. Veith, and an assistant researcher-teacher position (ATER) at the University of Toulouse in the group of L. Gorrichon, he got in 1996 a position at the CNRS in the group of J.-P. Majoral in Toulouse. He is currently "Chargé de Recherches". His research interests are in the synthesis and characterization of phosphorus-containing dendrimers and dendrons, their applications in catalysis, asymmetric catalysis, catalysis in water, and in their incorporation in inorganic materials. He is in charge of the technological platform Technopolym (polymer characterization).*

Jean-Pierre Majoral *is Emeritus Director of Research at the CNRS in Toulouse. His research interest is focused on the design and the properties of macromolecules such as phosphorus dendrimers and hyperbranched polymers. Main efforts are directed to the use of dendrimers in medicinal chemistry and material sciences. Emphasis is also laid on immobilization of molecular and macromolecular organo- and metal catalysts and their use for fine chemical synthesis. He is a member of several Academies of Sciences worldwide and an author of 545 publications and 45 patents.*

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1. Introduction

Dendrimers are macromolecules constituted of branches emanating radially from a central core. Dendrimers induce a large and increasing interest in the scientific community, due to the numerous properties they have in different fields, in particular for catalysis, for the elaboration of (nano)materials, and in biology/nanomedicine [1]. They are synthesized step-by-step, most generally by the repetition of a sequence of two reactions that induces a multiplication of the number of terminal functions, creating what is called a new "generation". Scheme 1 displays the principles for the divergent synthesis of dendrimers. The starting point is a multi-functional core, whose functions are activated, deprotected, or modified in the first step. A branched monomer is used in the second step to react with the modified core, affording the first generation dendrimer. The first generation has the same type of functions than the initial core, but the number of functions is multiplied, most generally by two, eventually by three [2], exceptionally by five [3]. If this sequence of reactions is absolutely quantitative, then the process can be used again, to afford the second generation, then the third, and so on. High generations have been attained for some dendrimers, generation 10 for PAMAM (polyamidoamine) dendrimers [4] and poly-L-lysine dendrimers [5], generation 12 for PPH (polyphosphorhydrazone) dendrimers [6], and very recently generation 13 for polytriazine dendrimers [7] and polyphenylene dendrimers [8]. Obtaining these high generations is a long process, but most of the properties of dendrimers can be attained with lower generations, most often not higher than generations 4 or 5.

A large number of publications and patents about dendrimers is related to catalysis. Indeed, dendrimers are considered in many cases as soluble supports of catalytic entities, most generally of transition metal complexes. The very first example in this field concerned a generation 1 carbosilane dendrimer ended by nickel derivatives, and used for the catalysis of the Kharasch addition [9]. The dendritic catalyst was less efficient than the monomeric catalyst, but it was proposed that only the dendrimer could be recovered and reused, using a membrane reactor. However, in most cases of re-uses of the catalysts, a bad solvent for the dendrimer is added to the reaction media after the catalytic experiments, to precipitate the dendritic catalysts. In most cases, this bad solvent is miscible with the solvent used for the catalysis, but it sufficiently modifies the media to induce the precipitation of the dendrimers. This is one of the major advantage when using a dendritic catalyst, the possibility to recover it easily, and to reuse it [10]. This aspect is particularly interesting when considering the