

STABILIZATION OF NANOPARTICLES BY MACROMOLECULES COMBINING PHOSPHORUS DENDRIMERS AND 15-MEMBERED TRIOLEFINIC AZAMACROCYCLES

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Introduction

Combinations of dendrimers¹ and macrocycles² started to be developed fifteen years ago³ to confer benefits coming from both macromolecular components to this original and unique nanoarchitecture. Such a concept has been extensively studied with a macrocycle at the core (*i.e.* porphyrins,⁴ phthalocyanines,⁵ cyclam⁶ or crown ethers⁷) but fewer reports deal with these macromolecules grafted at the periphery.⁸⁻¹⁰

The aim of this work is to demonstrate the ability to combine phosphorus dendrimers¹¹ and 15-membered azamacrocycles on the outer shell, phosphorus chemistry providing a fast and efficient tool to complete this kind of surface modification. These studies are carried out to demonstrate later on the interests to combine dendrimers functionalized with metalated macrocycles at the periphery in the field of catalysis.

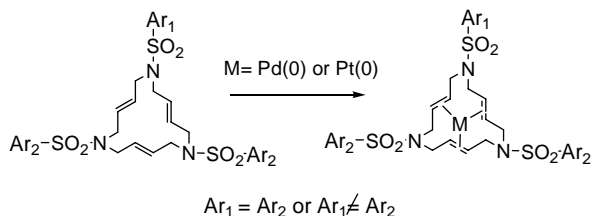
Experimental

Material. All manipulations were carried out with standard high-vacuum and dry-argon techniques. The solvents were freshly dried and distilled (THF and ether over sodium/benzophenone, pentane and CH₂Cl₂ over phosphorus pentoxide).

Synthesis. Modification of the periphery was achieved by mixing the dendrimer and a slight excess of macrocycles (*i.e.* 6.6 eq instead of 6 eq for the first generation) in dried THF. All reactions were monitored by ³¹P NMR. Macromolecules were purified by precipitation with pentane after having concentrated the crude mixture, followed by washings.

Results and Discussion

Some of us established the synthesis of 15-membered triolefinic macrocycles (Scheme 1). Through three different synthetic pathways tailoring of their aromatic substituents can be achieved.¹²⁻¹³ In addition, these macrocycles have the ability to coordinate transition metals through the three endocyclic double bonds (such as Pd(0) or Pt(0)).¹⁴ They were then used as recoverable agents in different catalytic processes, like in the Mizoroki-Heck reaction for instance.¹⁵ Access to homogenous nanoparticles was also reported with these kinds of stabilizing agents.¹⁶



Scheme 1. General representation of free 15-membered triolefinic azamacrocycles and their metalated analogs.

After convenient functionalization of the aryl groups and through our classical divergent synthetic methodology, we have successfully grafted various free azamacrocycles at the periphery of phosphorus dendrimers based on a cyclotriphosphazene core. From the first to the fourth generation, 6 to 48 peripheral substituents have been added on the outer shell to form a new series of high-molecular weight dendritic type macromolecules.

However, while trying to obtain the metalated analogs of our new series in order to determine the advantages of such dendritic shape macromolecules in catalysis, this "dual" architecture has been revealed itself as an excellent stabilizing agent for homogenous Pd(0)¹⁷ and Pt(0) nanoparticles (Figure 1).

In addition, the synthesis is reproducible and the distributions of the new species are quite narrow.

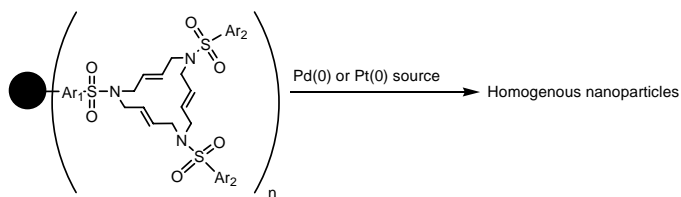


Figure 1. Dendritic macromolecules as efficient stabilizing agents for the formation of homogeneous nanoparticles ($n = 6, 12$ or 48).

Conclusion

Thus, in this work, we propose to demonstrate that phosphorus dendrimers and 15-membered azamacrocycles are versatile reagents for the synthesis of dendritic macromolecules. In addition these large macromolecules exhibit excellent ability to stabilize nanoparticles with different metals. Determination of their catalytic activities for different C-C bond coupling reactions is currently underway.

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