

Metallo dendrimers as a Catalyst: An Overview

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Introduction

Metallo dendrimers belongs to the class of large hyper-branched polymeric compounds with incorporated metal atoms. Metallo dendrimers are supramolecular moieties having novel physical, biological, Optical, electrochemical and catalytic properties. The initiation of incorporating metal ions in the dendritic framework (Figure 1) backs to the early 90's by Balzani and Newkome's [1-4].

Bi, Ge, Si, Zn, Fe, Pt, Pd, Er, Eu, Tb, CO, Cu, C60 [2,3,11-23] as a core, connector and peripheral group. It has been discussed with details in a review article by Newkome et al. [24] published in chemical reviews explanation about different types of metallo dendrimers and their chemical mechanism involved in it. This present overview attempts to touch the recent progress of metallo dendrimers in the field of catalysis.

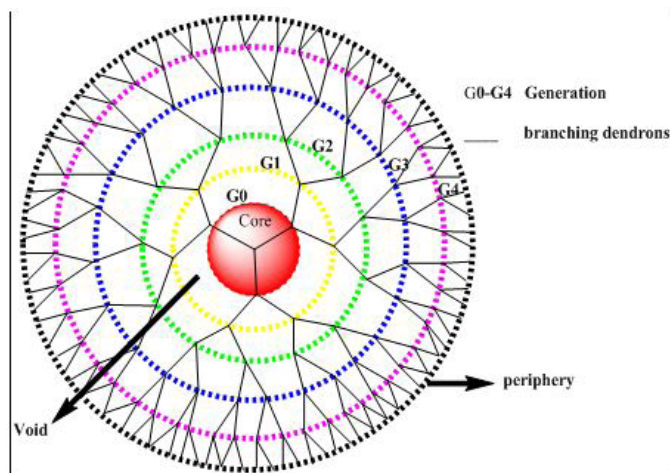


Figure 1: Schematic representation of dendrimeric framework.

The approaches used commonly either by internal metal complexation, use of metal branching centers or encapsulation at the specific binding site. In tradition, metal inclusion occurs after construction of dendritic framework in which metal's role as a connector as core or monomer, building block connectors, structural auxiliaries and branching centers. (Figure 2) After that, since 90's incredible work has been carried out in the field of metallo dendrimers with applications of synthetic novel materials as drug carriers [5,6], enzyme mimics [7,8], MRI contrast agents [9] and biocatalyst [10]. Metal ions that are used till now dates to Ru, Os,

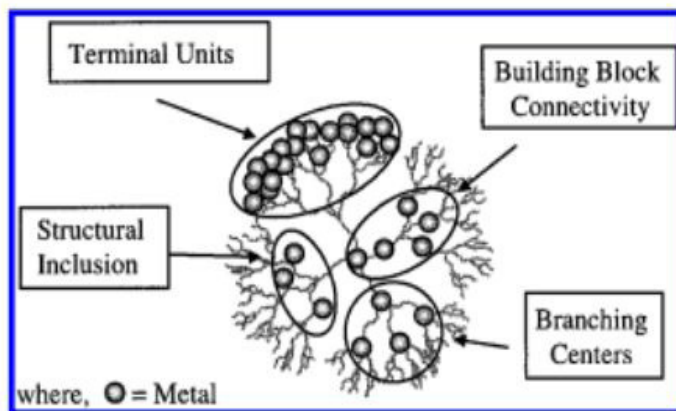
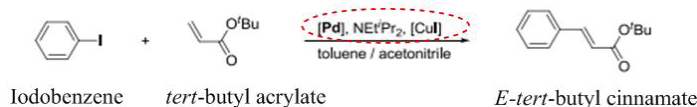


Figure 2: Potential uses and positioning of metals within dendritic structure [24].

Metallo dendrimers as a Catalyst

The Au nanoparticle were formulated by Au-PAMAM metallo dendrimer through *in situ* reduction using Na[BH₄] had set path for effective formation of nanoparticles by PAMAM-based dendritic stabilizers [25]. In another study amidoamine based dendrimers with peripheral Pd-Fe units has used in Heck reaction [26]. The study reports cooperative, positive effect of palladium containing amidoamine core metallo dendrimers in the Heck-Mizoroki cross coupling of iodobenzene with tert-butyl acrylate following heterogeneous carbon-carbon cross-coupling (Schema 1).



Scheme 1: Representative Heck-Mizoroki cross coupling using Pd containing amidoamine containing metallodendrimer as a catalyst [26].

In a very interesting study, the 4th generation PAMAM dendrimer with mixed Pd-Au and Pd-Pt NPs demonstrated more effective hydrogenation reaction in comparison to monometallic Pt or Pd catalyst [27-29]. The reason for such effective reaction may be due to rigid open structure of dendrimers and easy accessibility of substrate to active sites. Furthermore, the dendritic framework serves as a selectivity stage for the reactant and product, signifying high potential of dendrimer Nano catalyst as a control of catalytic chemical composition, solubility and recovery [28]. To study the effect of the dendrimer's generation on the catalytic activity El-Sayed in 2001 used PAMAM dendrimer-stabilized NPs in Suzuki cross-coupling reactions [30].

The first DAB dendrimer catalyst synthesized by Reetz in 1997, that reports the Heck reaction of bromobenzene and styrene to form *trans*-1, 2-diphenylethylene (Figure 3) yielded higher yield than traditional method [31].

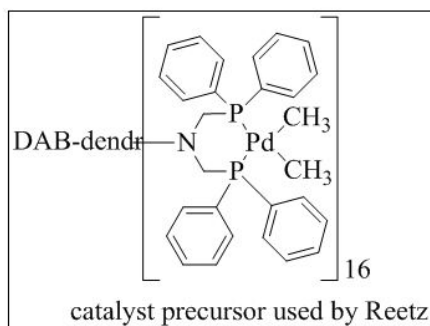


Figure 3: Representative DAB-Dendrimer for Heck reaction [31].

The same reaction using palladium-dendrimer complex supported by silica through three generation was reported by Alper et al. in 2000 [32]. However, the highest conversion factor was observed with 1st generation catalyst and higher turnover numbers (TONs) with 2nd generation catalyst after 6 hours. In contrast, Alper claims recyclability of the catalyst with no confirmational data proving the same.

Interestingly, Jacobsen et al. in 2000 represented the use of dendrimer catalyst in selective epoxidation reaction in addition to the epoxidation using Salen/metal complexes. In this work commercially, available Poly Amidoamine (PAMAM) was coupled with Cobalt-Salen moiety leading to the formation of 3rd generation dendrimers with *n*-Co-PAMAM (*n*=4/8/16). The epoxidation reaction was carried out with both monomeric catalyst and the dendrimers catalyst. It was found that there was no conversion taking place after 40 hours of the reaction, whereas the dendrimers catalyst showed 50% conversion with recovery of starting material and >98% enantioselectivity (ee). Further increase in generation of dendrimers and employment of the same in the reaction showed higher ee with a lower conversion rate. In contrast to the kinetic resolution of epoxides by Jacobsen, Bhyrappa et al. did shape selective epoxidation using metalloporphyrin dendrimers [33,34]. A more accessible double bond in non-conjugated dienes is possible with higher generation along with higher yield using metalloporphyrin dendrimers in comparison to monomeric tetraphenyl porphyrin.

Mizugaki et al. in 1999 studied selective hydrogenation of dienes to monoenes using DAB-dendr-[N(CH₂PPh₂)₂PdCl₂]₁₆ (DAB-dendr = 1,4-diaminobutane polyamino) [35]. The metallodendrimers catalyst was synthesized by reaction of commercially available dendrimer DAB-dendr-(NH₂)₁₆ with Ph₂PCH₂OH. The terminal phosphines were complexed using [PdCl₂(PhCN)₂] to give Pd-metallodendrimer catalyst. The catalytic activity was considerably higher than the traditional monomeric catalyst PhN(CH₂PPh₂)₂PdCl₂. However, the dendrimer catalyst selectively hydrogenated cyclopentadiene to cyclopentene, whereas, the traditional catalyst hydrogenated both double bonds. However, the activity of dendrimer catalyst is lower than Pd/C or Pd/Al₂O₃, which is not reusable whereas the dendrimers catalyst can recover by centrifugation and could be reused with minor loss in its activity. The another metallodendrimer synthesized by Jayaram et al. with poly(alkyl-aryl-ether) core and phosphine terminal groups complexes using [Rh(COD)Cl₂] (Figure 4) where a steady increase in TONs was observed with increasing generation [36]. Notably the highest TONs of 900 in a 60-minute cycle was recorded by the metallodendrimer catalyst whereas the monomeric catalyst reached only just 450 in 60 minutes. In a similar method Zhan et al. used the same core by combining with [Ru(COD)₂][BF₄] for asymmetric hydrogenation. The catalyst was reused five times with same enantioselectivity [37].

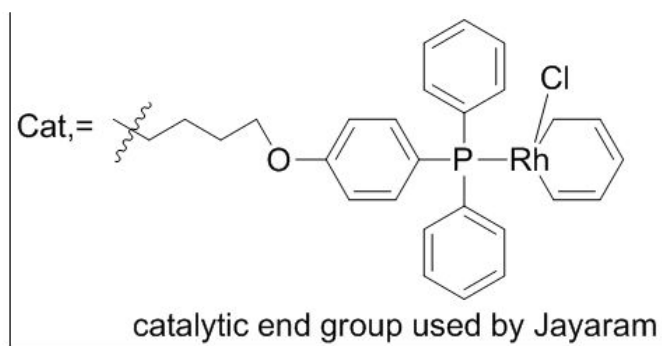


Figure 4: Representative $[Rh(COD)Cl_2]$ complexed poly(alkyl-aryl-ether) metallodendrimer.

In 2007 Scrimin et al. used Zn^{III} complexes of triazacyclononane functionalized DAB dendrimer as transphosphorylation catalyst for cleavage of RNA model substrate HPNPP [38] (Figure 5).

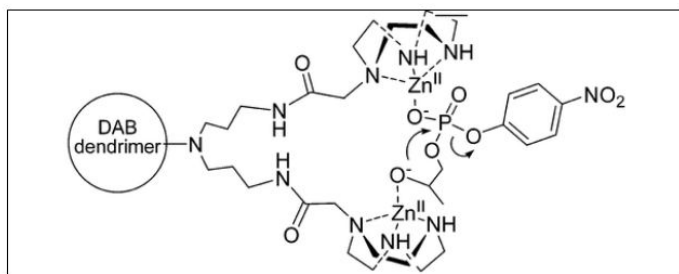


Figure 5: Representative structure of Zn^{III} complexes of triazacyclononane functionalized DAB dendrimer with two metal centers [38].

In summary, it could be stated that the metallodendrimers for catalysis is not confined to few examples represented. The potential application of dendrimers, metallodendrimers and bio-metallodendrimers is impactful and extensive not only in catalysis but also in dendrimer based medicines, gene delivery, MRI agents, light emitting diodes, chemical sensors, molecular recognition, and as a biomimetic agent.

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