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## A Career In Catalysis: Didier Astruc

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**Keywords:** electron reservoir, electrocatalyst, olefin metathesis, micellar nanoreactor, supramolecular nanocatalysis, transition metal nanoparticle, hydrogen, dendrimer.

**Abstract:** We are honored to reflect on and highlight in this account Didier Astruc's achievements in various aspects of catalysis stretching from his concept and design of organoiron electron reservoir complexes and application to redox and electrocatalysis to his dendritic constructions leading to their use in dendritic catalysis, supramolecular nanocatalysis and energy-related catalysis. It is at the end of the 70's that Didier Astruc isolated the first stable, well-characterized 19-electron sandwich complex as electron reservoir and disclosed their catalytic applications. At the same time, he developed an original system of arene polyfunctionalization to star-shaped molecules and dendrimers that he then decorated with catalysts for oxidation, electrocatalysis, polymerization by ROMP and other olefin metathesis reactions. After disclosure by his group of click metallodendrimers during the first decade of this century, he used them as templates for synthesis of well-defined ultra-small metal nanoparticles extremely active in catalysis for olefin hydrogenation and C-C bond formation using extremely low catalytic amounts. During the last 15 years, Didier Astruc designed dendritic micellar nanoreactors for molecular, ionic and nanoparticle catalysis, autocatalysis and nanozyme catalysis. Recently, his interest focused *inter alia* on nanocatalyzed hydrogen (H<sub>2</sub>) production with very efficient endo- and exoreceptors, and CO<sub>2</sub> fixation, a field of sustainable energy in which he and his group are currently very active.

## INTRODUCTION

Didier Astruc (Figure 1), born in Versailles, followed education in Rennes where he prepared two doctorate theses in organometallic chemistry under the guidance of René Dabard. After his first doctorate, he took a teaching position at the Technological Institute of Saint-Nazaire, quickly becoming a young Master Lecturer there at 25 years old, while completing his "State" doctorate in Rennes.



**Figure 1.** Prof. Didier Astruc.

Thereafter, Didier was a NATO post-doctoral fellow at MIT in Cambridge, Massachusetts, with Dick Schrock. Then, he was appointed at the CNRS in Rennes first as Chargé de Recherche then, at 33 years old, as Maître de Recherche, where he developed his seminal work on 19-electron Fe(I) complexes and catalysts.<sup>1</sup> A few years later, he accepted a professorship position at the University of Bordeaux, where he became a Member of the Institut Universitaire de France in 1995 and an exceptional class Professor in 1999. During 1990-1991, he spent a sabbatical leave at UC Berkeley with K. Peter C. Vollhardt with whom he developed a collaboration in electrocatalysis.<sup>2</sup> He started to write there his book on electron transfer for which Henry Taube included a very complimentary preface.<sup>3</sup> In 2001, he authored a French organometallic chemistry textbook that was translated into several languages and extended to catalysis in 2007 and 2013.<sup>4</sup> He edited several books, notably with Wiley “*Modern Arene Chemistry*” (2001) and “*Nanoparticles and Catalysis*” (2008), and he recently served as Guest Editor of the 2020 *Chemical Reviews* Thematic Issue on Nanoparticles in Catalysis.<sup>5</sup>

Didier is a member of the French, German (Leopoldina) and various European Academies of Sciences and a Fellow of the Royal Society of Chemistry and ChemPubSoc Europe. He received *inter alia* the Humboldt Award (1995), Iberdrola Award (1996), several awards from

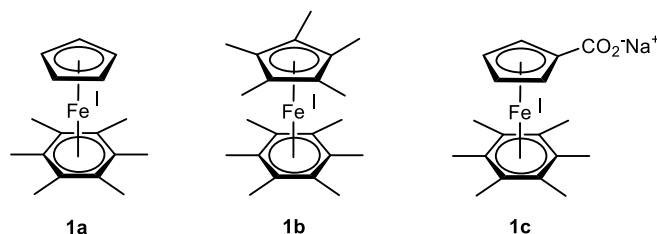
the French Chemical Society, especially the Le Bel Award (2000) and the Italian-French Chemical Society Award (2009). He was remarked as teacher, being distinguished by the award of the Teaching Division of the French Chemical Society in 2016. He was a Watt Lecturer at Austin, Texas (1993), a Karl Friedrich Gauss Professor of the University of Göttingen (2008), “3M Named Lecturer” of the University of London, Western Ontario (2009), invited Professor in the Universities of Santiago (1984), Heidelberg (1992), Mexico (2000), Sichuan at Chengdu (2014 and 2016), and Anhui at Hefei (2018). So far, he has given over 450 research lectures in the five continents and published over 580 research articles. He has been on the Thompson-Reuters list of the 100 chemists having the highest impact of their publications between 2000 and 2010, and on the Clarivate Analytics lists of Highly Cited Researchers every year since 2015.

Didier educated and trained generations of undergraduates, doctoral students and postdocs that currently contribute as new scientists in academia, national laboratories, and industry all around the world. Didier is not only a research supervisor, but he is also an incredible mentor who inspires, motivates, and supports his students throughout their careers, way beyond their PhD defense, and often becomes their long-term collaborator.

## **REDOX CATALYSIS AND ELECTROCATALYSIS WITH ORGANOIRON ELECTRON RESERVOIRS**

In the 1970's, the 18-electron rule was still considered as a general trend for the first-row late transition-metal complexes in terms of complex stability (see the first chapter of Didier's book<sup>4</sup> for the validity of the 18-electron rule).<sup>4,6,7</sup> Thus, the discovery by Didier and his group in Rennes in the late 70's of the stability, including X-ray crystal structure, Mössbauer and <sup>1</sup>H NMR spectroscopies and mass spectrometry of a whole family of stable truly 19-electron d<sup>7</sup> Fe(I) iron complexes was a landmark in the field.<sup>1</sup> Didier became well known in the organometallic and catalysis community with his seminal concept of electron reservoirs using this first well-characterized 19-electron organo-iron complexes.<sup>1</sup> That publication not only set the stage for iron-based redox catalysts and electrocatalysts, but also for the construction of star-shaped molecules and giant dendrimers that later allowed him to develop metallodendrimer catalysis.<sup>8</sup> In the late 90's, Didier addressed the analogy between these macromolecules and gold-thiolate nanoparticles, then developed a variety of transition-metal nanoparticles and their interest in nanocatalysis.<sup>5,9</sup>

Didier applied early on his concept of electron reservoir to stoichiometric and catalytic electron transfer processes.<sup>1,10-14</sup> Indeed, the prototypal 19-electron complexes [Fe(I)Cp'(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)] (**1a**: Cp' = Cp = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>; **1b**: Cp' = Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) were found by He(I) photoelectron spectroscopy to be the most electron-rich neutral molecule still known to-day, with ionization potential values down to 4.21 eV for **1b** (Figure 2).<sup>15</sup>



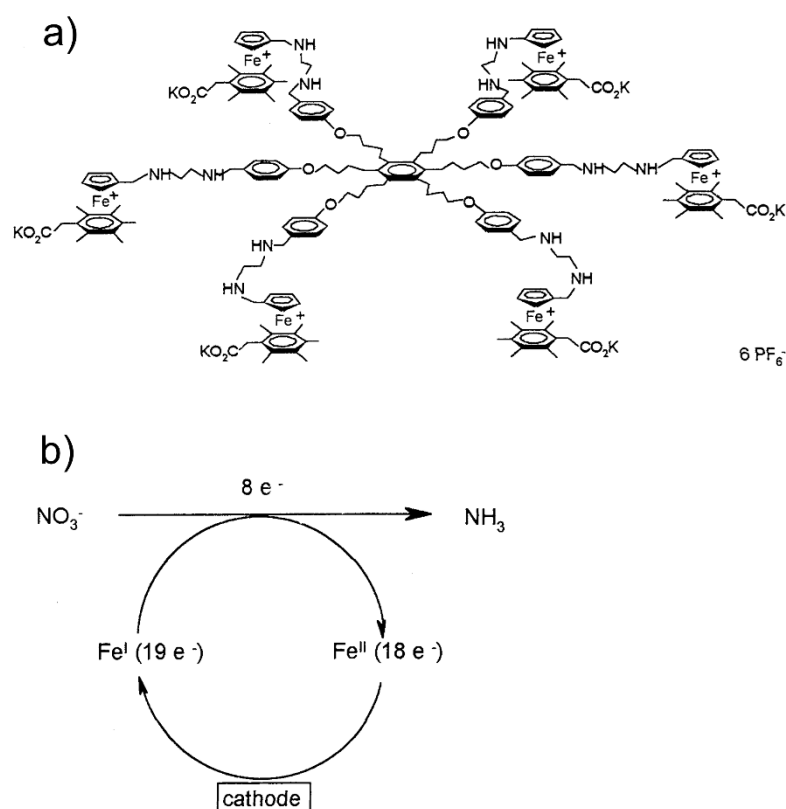
**Figure 2.** Well-characterized prototypal 19-electron d<sup>7</sup> Fe<sup>I</sup> complexes, that are thermally stable and very active in redox catalysis and electrocatalysis.

Mössbauer and electron spin resonance (ESR) spectroscopy studies showed that the orbital of the 19<sup>th</sup> electron is essentially metal-centered,<sup>1,16</sup> whereas it is only about half on the metal in isolobal cobaltocene<sup>17</sup> whose redox potential is accordingly one volt lower than that of **1a**. The Mössbauer spectra showed that the 19<sup>th</sup> electron was in the antibonding metal e\* orbital with temperature-dependent quadrupole splitting (QS) indicating thermal population of the upper Kramer's doublet. In addition, the QS hysteresis of this temperature dependence was very sensitive to the nature and number of alkyl substituents on the rings showing the molecular-lattice cooperativity<sup>1,10,13</sup> of these “memory devices” (i.e. for a given temperature, the QS value is different depending on whether the temperature rises or falls).<sup>18,19</sup> Examples of the reductant properties of these Fe(I) 19-electron complexes included *inter alia* for **1a**, reduction of dioxygen to superoxide radical anion (O<sub>2</sub><sup>•-</sup>)<sup>11</sup> with dramatic salt effects.<sup>12</sup> The related role of O<sub>2</sub><sup>•-</sup> and derived oxygen radicals towards living cells<sup>20</sup> and this salt effect intrigued Didier, and that was the opportunity for him to develop close and fruitful contacts and collaboration with an illustrious organic chemist, Bianka Tchoubar,<sup>21</sup> a former student of Marie Curie who had been the Director of a CNRS research center in Thiais, near Paris.<sup>22</sup>

Other useful electron-transfer reactions of **1a** and analogues include the selective one-, two- and three-electron reduction of C<sub>60</sub>,<sup>23</sup> stabilization of monoanionic gold nanoclusters (**1b** better than **1a** due to bulk),<sup>24</sup> and their use with air to generate *N*-Heterocyclic Carbenes (NHC)<sup>25</sup> that are valuable ligands in organometallic catalysis. Another useful property of the electron-reservoir complexes, particularly **1b**, is their ability to serve as references in non-aqueous

electrochemistry,<sup>26</sup> due to the lack of reliably precise results with the ferrocene reference regarding interactions with electrolyte counter anions and nucleophilic solvents.<sup>27</sup>

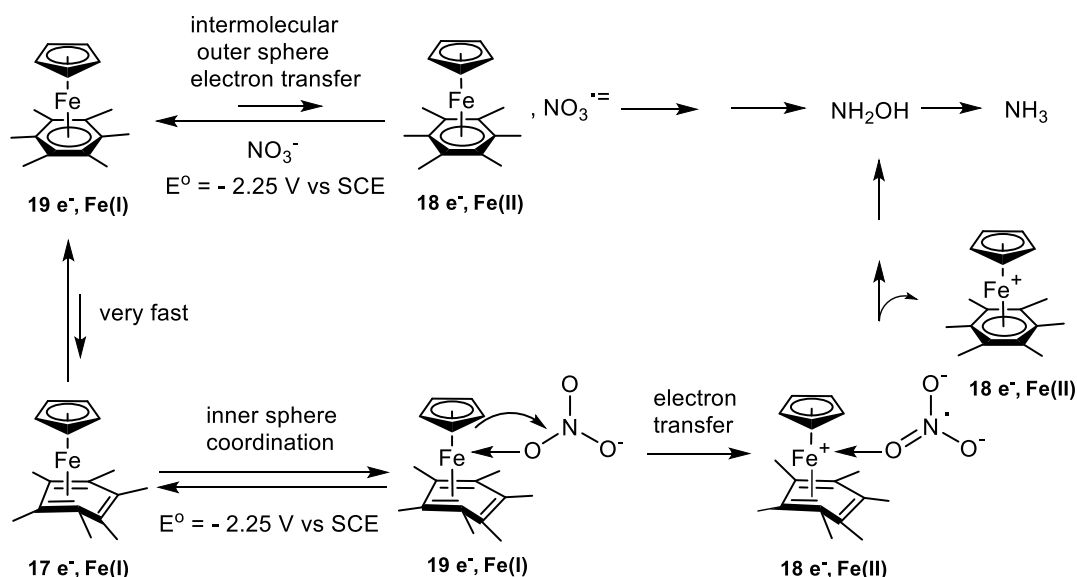
The stability and robustness of the organo-iron electron reservoir complexes, their strong reductant abilities, the easy functionalization (such as carboxylation) of their ligands,<sup>28</sup> and the control of their redox potentials that can be engineered by the choice of the number and location of methyl groups on the ligands are all crucial properties in redox catalysis and electrocatalysis.<sup>3</sup> Didier was inspired by pioneers in these fields including Laviron<sup>29</sup> (with whom he collaborated for his early thesis publications following an intern in Dijon) and Savéant<sup>30</sup> in France, Taube,<sup>31</sup> Kochi<sup>32</sup> and Marcus<sup>33</sup> in the U. S., and Hush in Australia.<sup>34</sup> The series of fully reversible Fe(I/II) redox systems, derived from the electron-reservoir CpFe(arene) family containing a solubilizing carboxylate group on either ligand, with redox potentials between -1.5 and -1.8 V vs. SCE were shown to be active redox catalysts on Hg cathode for the reduction of nitrates and nitrites to ammonia in basic aqueous medium (Figure 3).<sup>28,35</sup>



**Figure 3.** Redox catalysis by dendritic electron-reservoir Fe(II/I) sandwich complexes of the cathodic reduction of nitrates (and nitrites) to ammonia under ambient conditions in basic aqueous medium. a) Example of the family of water-soluble Fe(II) redox catalysts of nitrate and nitrite cathodic reduction; b) general mechanism of the redox catalysis (for outer-sphere and inner-sphere mechanistic possibilities, see Scheme 1). Substrate reduction occurs in solution, and the reduced active catalytic form is regenerated by reduction of Fe(II) to Fe(I) at the cathode. For

general aspects, examples and applications of redox catalysis, see ref. 3, chapter 7. Reproduced with permission from ref 35. Copyright 2002 Elsevier.

Among the various possible electrochemical techniques able to determine the reaction kinetics, cyclic voltammetry using Ficks' equation applicable to a planar electrode (low time scales allowing a thin diffusion layer approximating planarity) turned out to be the most practical one. Under these conditions, the kinetic constant  $k$  of the homogeneous reduction was easily derived, in the Astruc group, from the ratio between the cathodic current intensity  $I_k$  in the presence of the catalyst ( $I_k$  at the plateau observed under kinetic control; scan rates between 100 and 300 mV/s) and the intensity  $I_d$  in its absence, provided by Nicholson and Shain.<sup>36</sup> A series of these water soluble iron complexes bearing carboxylate groups (such as **1c**, Figure 2) and the rigid  $C_6Me_6$  or  $C_6Me_5CH_2CO_2^-$  ligand, showed a linear relationship between  $\log k$  and  $E^\circ$  that corresponded to a Marcus-type relationship<sup>33</sup> showing an outer-sphere rate-limiting electron transfer step (mediation). For bulkier catalysts, the electron-transfer rate was much slower.<sup>35</sup> Since the 17 to 19-electron interconversion between the  $\eta^4$ - and  $\eta^6$ -arene ligands is fast, a possible inner-sphere contribution (redox catalysis)<sup>30,31</sup> involving transient coordination of the oxygen atom of the nitrate onto Fe(I) was not excluded, however (Scheme 1).

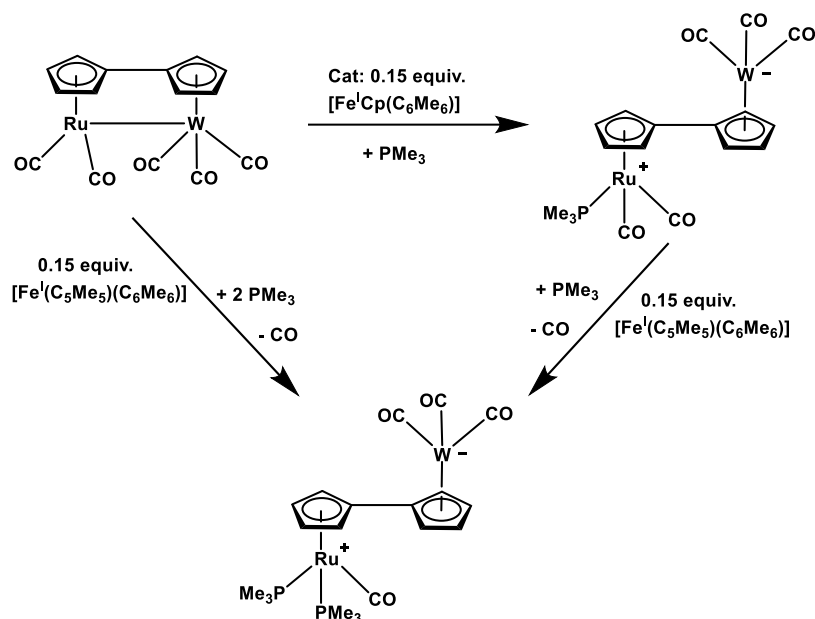


**Scheme 1.** Compared outer-sphere (top) and inner-sphere (bottom) mechanisms for the redox catalysis of the cathodic reduction of nitrate (or nitrite) to ammonia. The neutral complex reducing nitrate in the scheme is the 19-electron Fe(I) complex (top left). However, fast equilibrium with a 17-electron Fe(I) form in solution with a partly uncoordinated arene ligand (bottom left) was also proposed to possibly allow nitrate coordination towards inner-sphere reduction (these possibilities were discussed with Henry Taube after a seminar by Didier in Stanford

University in 1991). For distinction between outer-sphere and inner-sphere mechanism, see ref. 3, chapter 1 and ref. 31. Reproduced with permission from ref 35. Copyright 2002 Elsevier.

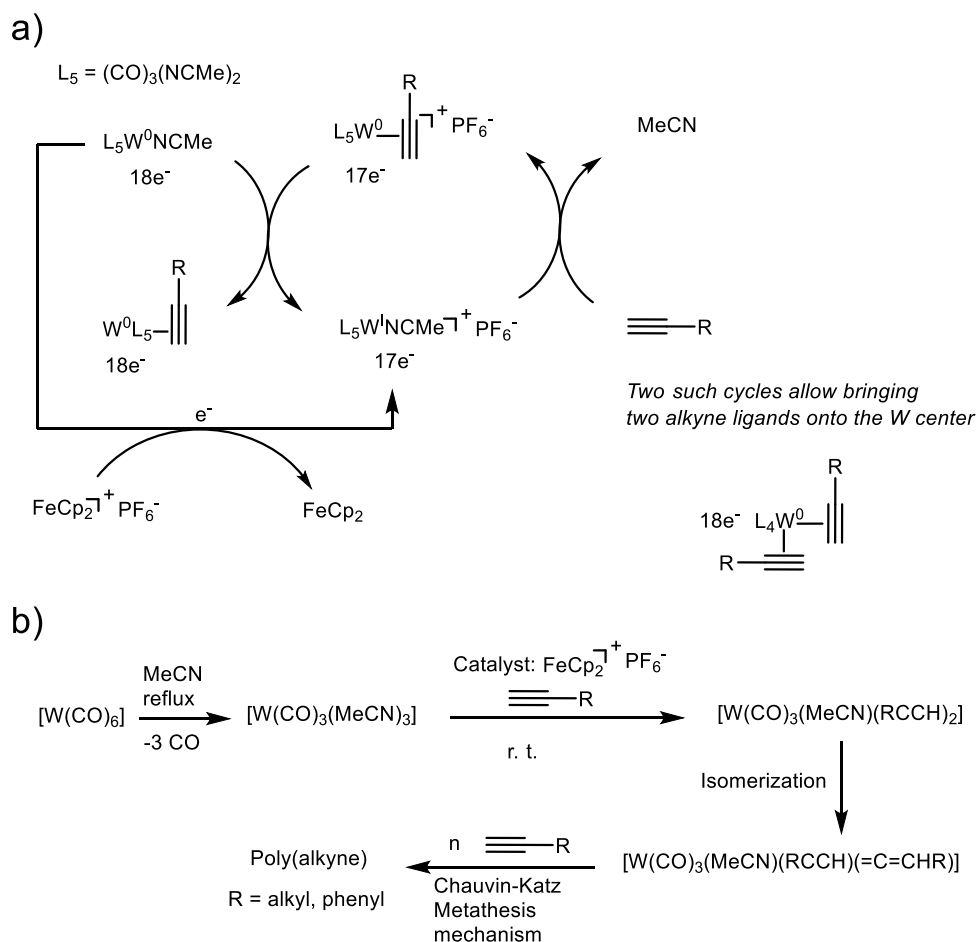
The other type of electrocatalyzed reaction is Electron-Transfer-Chain (ETC) catalysis that can involve a large number of classic organic and inorganic reactions such as substitution, chelation, insertion, etc. in which, contrary to redox catalysis, there is generally no change of oxidation state between the substrate and the product.<sup>3,30,32,37</sup> A review of the catalytic use of electron shuttles in organic chemistry has been published in 2014 by Studer and Curran in which various examples of ETC-catalyzed organic reactions are reported.<sup>38</sup> This type of electrocatalyzed (ETC) reactions does not necessarily involve electrochemistry. Indeed, such ETC-catalyzed reactions were successfully conducted by Didier and his group in solution using the prototypical electron reservoir complexes **1a** and **1b** that are very efficient initiators of ETC catalysis.<sup>2,37</sup> ETC-catalyzed reactions were pioneered by Henry Taube in 1954 with several reports including the most interesting catalysis by Pt(III) of exchange reactions of  $\text{PtCl}_4^{2-}$  and  $\text{PtCl}_6^{2-}$ .<sup>39</sup> The interest of the electron-reservoir complexes as ETC catalysis initiators is their extremely negative Fe(I/II) redox potential<sup>1,10,13,15</sup> allowing a very broad range of ETC catalyzed reactions. For instance, 1% of **1a** could cleanly catalyze the quantitative exchange by three P-donors ligands such as  $\text{P}(\text{OMe})_3$  of the arene ligands in  $[\text{CpFe}(\text{II})\text{arene}]^+$  salts in which these arene ligands were benzene or mesitylene, i.e. less electron rich than  $\text{C}_6\text{Me}_6$ , the reaction being consequently fast because of the exergonicity of the redox initiation step involving **1a** with the complex salts.<sup>40</sup> Another noteworthy example was that of Vollhardt's homo- and heterobinuclear fulvalene (Fv) complexes with the selective use of **1a** vs. **1b** in the ETC catalytic exchange of carbonyl ligands in the complexes  $\text{FvM}^1\text{M}^2(\text{CO})_n$  ( $\text{M}^1, \text{M}^2 = \text{Mo}, \text{W}, \text{Fe}, \text{Ru}, n = 4-6$ ).<sup>2,41</sup> In the homobinuclear complexes, ETC catalysis using 1% **1a** led to quantitative exchange of CO by  $\text{PMe}_3$  at a single metal center providing zwitterionic metal complexes in which the  $\text{M}^1 - \text{M}^2$  bond was cleaved.<sup>41</sup> On the other hand, in heterometallic complexes such as the FvRuW complex, ETC initiation by 1% of **1a** led to the zwitterionic complex in which only one CO was exchanged by  $\text{PMe}_3$  at the Ru center, whereas with the more powerful initiator **1b**, exchange of 2 CO's by 2  $\text{PMe}_3$  ligands was obtained.<sup>2</sup> This example illustrated the importance of the value of the redox potential of the ETC initiator and the interest of a library of initiators with different numbers of Me groups on the ligands in ETC catalysis (Scheme 2).





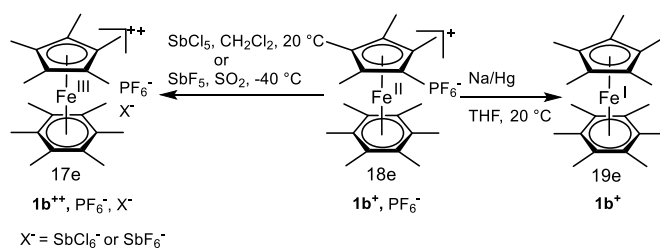
**Scheme 2.** ETC Catalyzed  $\text{PMe}_3$  ligand addition in the fulvalene heterobimetallic complex  $[\text{RuW}(\eta^{10}, \mu^2\text{-C}_{10}\text{H}_8)(\text{CO})_5]$ . The number of substituted CO ligands (0 or 1) depends on the Fe(II/I) redox potential of the electron-reservoir ETC catalyst (**1a** vs. **1b**). Reprinted with permission from ref 2. Copyright 1994 Wiley-VCH).

The electron reservoir systems such as **1a** and **1b** parallel the ferrocene-ferricenium system on the oxidation side. Therefore, Didier's group used ferricenium, a 17-electron complex, as an ETC catalyst of the MeCN/alkyne ligand exchange at the level of the labile 17-electron form coupled with the precursor  $[\text{W}(\text{CO})_3(\text{MeCN})_3]$  of terminal alkyne polymerization according to the Chauvin-Katz metathesis polymerization mechanism.<sup>42,43</sup> Whereas heating to  $100^\circ\text{C}$  was required to generate a tungsten vinylidene catalyst from this precursor and a terminal alkyne,<sup>43</sup> addition of a catalytic amount of ferricenium salt vs. the W precursor made the same alkyne polymerization possible, rapidly under ambient conditions.<sup>44</sup> The proposed mechanism for the acceleration step is shown in Scheme 3a, and the sequence of reactions including the acceleration step with the Fe(III) salt in scheme 3b.<sup>44</sup>



**Scheme 3.** Proposed mechanism for the very strong acceleration by the electron-transfer-chain (ETC) catalyst (ferricenium) of the metathesis polymerization of terminal alkynes. a) ETC-catalyzed MeCN substitution by alkyne (the rate-acceleration step); b) reaction balance for the catalyst from its precursor to its active form followed by (bottom) metathesis catalysis of alkyne polymerization. For a review of ETC catalysis, see ref. 3 (chapter 6), ref. 4 (chapter 5, pp. 127-131) and ref. 37.

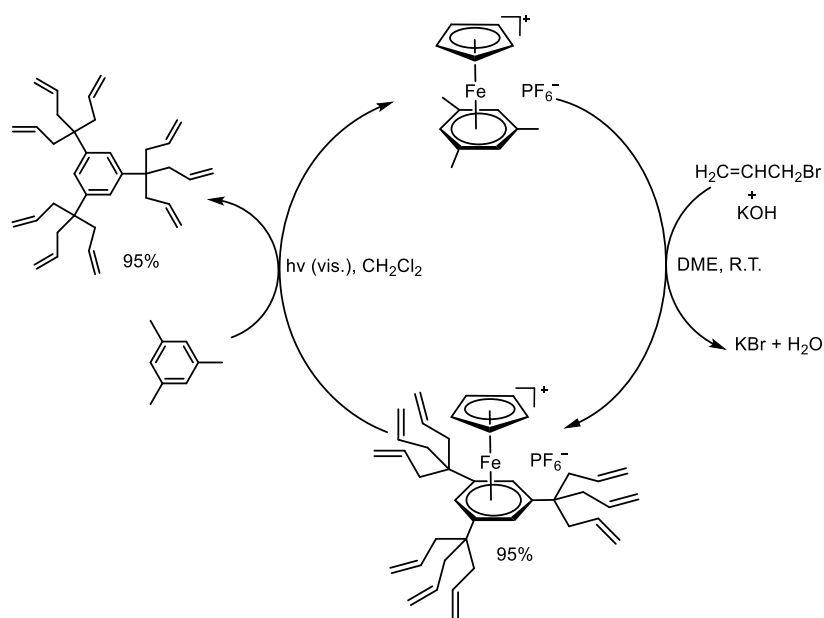
Ferricenium salts are modest, yet efficient oxidants when the substrate can be easily oxidized. The need of stronger oxidant may sometimes be required, however, for substrates that cannot be oxidized by ferricenium salts. Although the salts of the family of  $1^+$  were believed to be impossible to oxidize because of their positive charge, the Astruc group succeeded in oxidizing the Fe(II) form  $1b^+$  to  $1b^{2+}$  in  $\text{SO}_2$  or MeCN using  $\text{SbF}_5$  or  $\text{SbCl}_5$ , and the 17-electron complex  $[\text{Fe}^{\text{III}}(\eta^5\text{-C}_5\text{Me}_5)(\eta^6\text{-C}_6\text{Me}_6)](\text{PF}_6)(\text{SbCl}_6)$ , a very strong oxidant,<sup>45</sup> (Scheme 4) could even be isolated and used as oxidant and redox catalyst or ETC catalyst for various reactions.<sup>46</sup>



**Scheme 4.** Syntheses of the 19e  $d^7$  Fe(I) electron reservoir **1b** and of the 17e  $d^5$  Fe(III) reservoir of electron hole **1b**<sup>++</sup>  $\text{PF}_6^-$ ,  $\text{SbX}_6^-$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) from the 18e  $d^6$  Fe(II) sandwich complex **1b**<sup>+</sup>,  $\text{PF}_6^-$ .

## DENDRITIC CATALYSTS AND DENDRIMERS IN MOLECULAR CATALYSIS

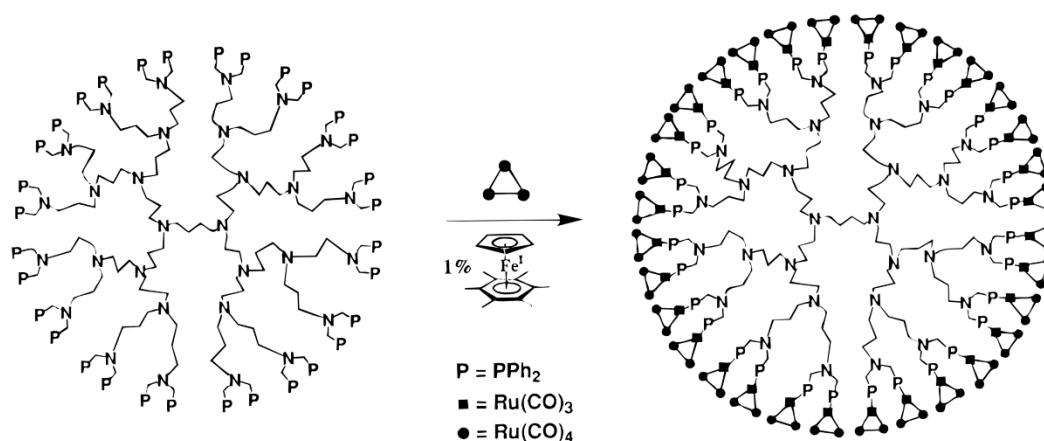
A unique discovery of Didier and his group was the one-pot iterative  $\text{CpFe}^+$ -induced polyalkylation and polyfunctionalization of polymethylbenzenes leading to star-shaped<sup>47,48</sup> and dendritic molecules,<sup>49-52</sup> also applied to pentamethyl cobalticinium<sup>50</sup> and decamethyl rhodocenium salts<sup>51</sup> with formation in one pot of 10 or 20 branches, respectively. Using this strategy, the phase-transfer catalyzed  $\text{CpFe}^+$ -induced mesitylene nona-allylation<sup>52</sup> has been the most used example in the Astruc group for further dendritic construction<sup>53,54</sup> towards catalytic applications.



**Scheme 5.** High-yield cyclic  $\text{CpFe}^+$ -induced nona-allylation of mesitylene. The cationic charge of the Fe(II) complex activates benzylic deprotonation, followed by nucleophilic substitution of  $\text{Br}^-$  in  $\text{CH}_2=\text{CHCH}_2\text{Br}$ ; this sequence spontaneously proceeds *in situ* 9 times under ambient conditions.

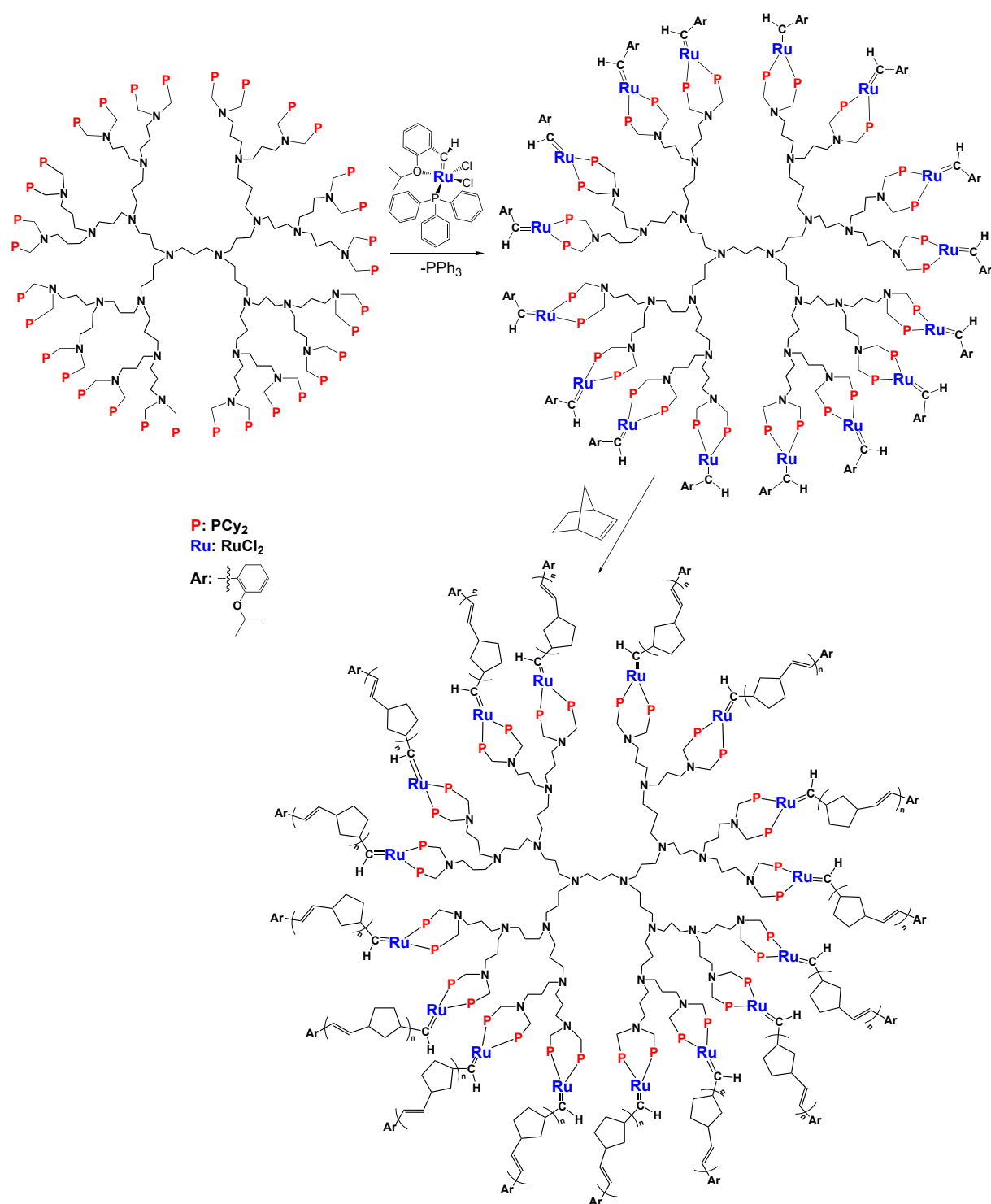
The 12-electron  $\text{CpFe}^+$  moiety used in mesitylene activation of the 9 C-H bonds and allylation could also be recycled upon photolysis with visible light of the nona-allyl complex in the presence of mesitylene, regenerating the complex  $[\text{FeCp}(\text{mesitylene})]\text{PF}_6^-$  (Scheme 5). These  $\text{CpFe}^+$ -induced perfunctionalization reactions pioneered in his 1979 paper,<sup>1</sup> were the beginnings of Didier's research on dendrimers (*vide infra*) that he further used in catalysis. It is around that time, in the early 1980's, that the first well-defined dendrimers were reported by Tomalia<sup>55</sup> and Newkome,<sup>56</sup> whereas their use in catalysis appeared a decade later with the seminal work by the group of Van Koten<sup>57</sup> and others.<sup>58</sup> Didier also became interested in the redox properties of his metallodendrimers in the 1990's (*vide infra*) and in catalysis herewith in the early 2000's. For instance, the nona-tri(hexyl) ammonium salt of the peroxophosphotungstate  $[\text{PO}_4\{\text{WO}(\text{O}_2)_2\}_4]^{3-}$  was derived from the nona-allyl arene and characterized in particular by atomic force microscopy (AFM) (height: 2.9 nm). This composite proved to be, under ambient conditions, an efficient and fully recyclable catalyst for the epoxidation of olefins by  $\text{H}_2\text{O}_2$  in quantitative yield in water/ $\text{CDCl}_3$  and the selective oxidation of thioanisole to the sulfone.<sup>59</sup>

Didier's group decorated phosphine-terminated dendrimers with carbonyl clusters using ETC catalysis. Dendrimers terminated by 32 or 64  $\text{CH}_2\text{PPh}_2$  groups were shown to react under ambient conditions with the cluster  $[\text{Ru}_3(\text{CO})_{12}]$  in slight excess in the presence of 0.1 equiv. of the ETC catalyst **1a** in THF. These reactions, easily characterized in particular by  $^{31}\text{P}$  NMR, led to the coordination of the 32 or 64 dendritic phosphine branches to a ruthenium atom of the cluster  $[\text{Ru}_3(\text{CO})_{11}]$  upon selective substitution of a single CO ligand *per* cluster unit (Scheme 6).<sup>60</sup> Mono-electronic reduction of the cluster  $[\text{Ru}_3(\text{CO})_{12}]$  by **1** is exergonic, because the potential of irreversible reduction of  $[\text{Ru}_3(\text{CO})_{12}]$  is 0.87 V less negative than the standard redox potential of the system  $\mathbf{1a}^+/\mathbf{1a}$ , making the ETC catalytic process favorable.<sup>37</sup>



**Scheme 6.** ETC catalyzed introduction of Ru carbonyl clusters at the dendrimer periphery by selective CO exchange by dendritic phosphine ligand. Reprinted with permission from ref 60. Copyright 2000 American Chemical Society.

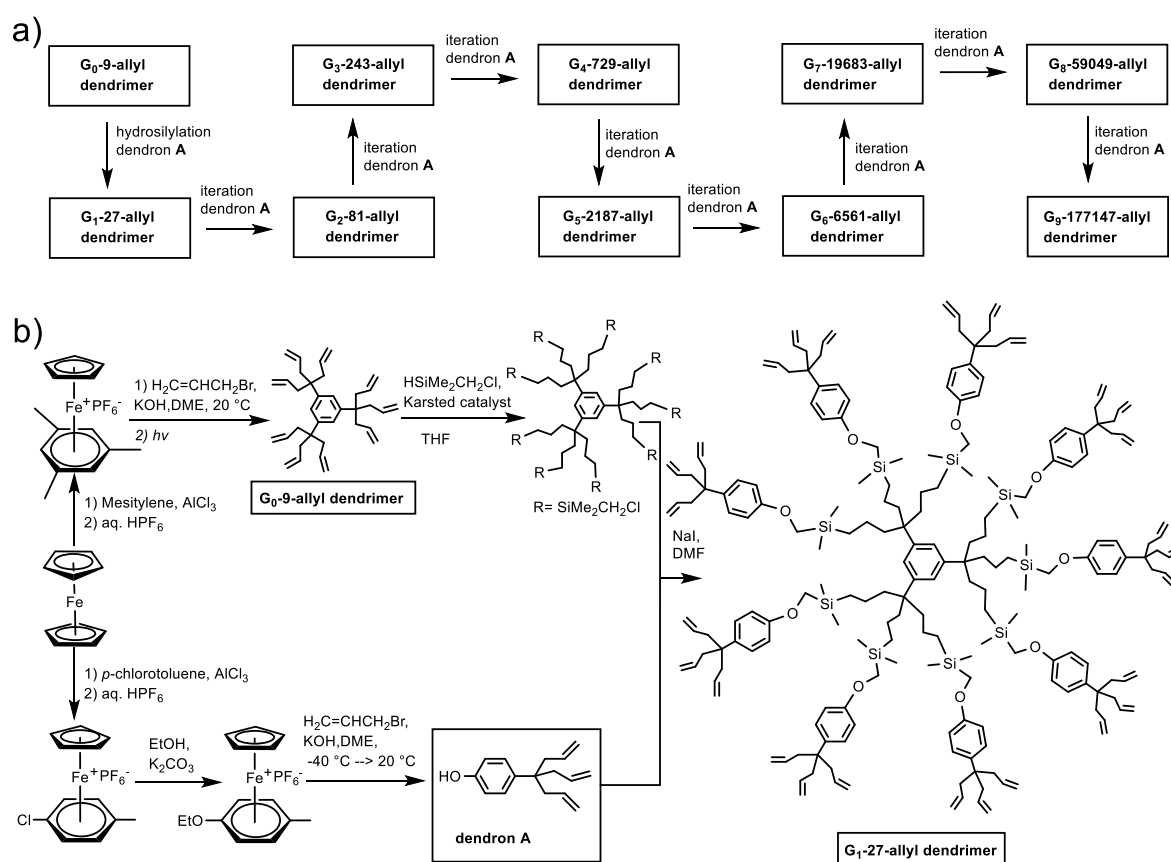
The discovery of the olefin metathesis mechanism by Chauvin and subsequently of efficient olefin metathesis catalysts by the Schrock and Grubbs groups<sup>42,61-63</sup> that led to the 2005 Nobel Prize allowed a major breakthrough in macromolecular chemistry.<sup>64,65</sup> Application of metathesis reactions to dendrimer chemistry provided the finding of new structures such as cages as well as dendrimer functionalization in the Astruc group.<sup>63</sup> The ring-opening metathesis polymerization (ROMP) reaction<sup>64,65</sup> was applied to the polymerization along the dendrimer branches yielding dendritic polynorbornenes.<sup>66</sup> New monomeric and several generations of dendrimer-terminated Ru-benzylidene complexes were synthesized and used at room temperature as ROMP catalysts for norbornene polymerization. It was worth noting that the catalysis was faster with the dendritic Ru-benzylidene complexes when comparing with the monomeric model, presumably because the metal-ligand bonds are more fragile in the metallodendrimers than in the monomer due to interbranch collisions around the Ru center in the metallodendrimers (Figure 4). Polymerization rates decreased, however, upon increase of the dendrimer generation due to steric effects.<sup>66</sup> Indeed, generally the dendritic effect in catalysis is positive when comparing the dendritic catalysts with the monomeric species, but it is negative upon growing on dendrimer generation due to the increasing steric effects at the dendrimer's periphery.<sup>58</sup> Nanozyme dendritic catalysts are an exception (*vide infra*).



**Figure 4.** a) Incorporation of a Ru benzylidene ROMP catalyst at the periphery of dendrimers (planar representation); b) ROMP of norbornene in the branches of the dendritic ROMP catalyst.

The nona-allyl dendrimer core synthesized by CpFe<sup>+</sup>-induced nona-allylation of the mesitylene complex followed by demetallation (Scheme 5) is a highly branched symmetrical molecule that was used by Didier's group as a dendritic core for the synthesis of a family of giant organic dendrimers.<sup>53,54</sup> Hydrosilylation of the allylic branches with HSi(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>Cl using Karstedt

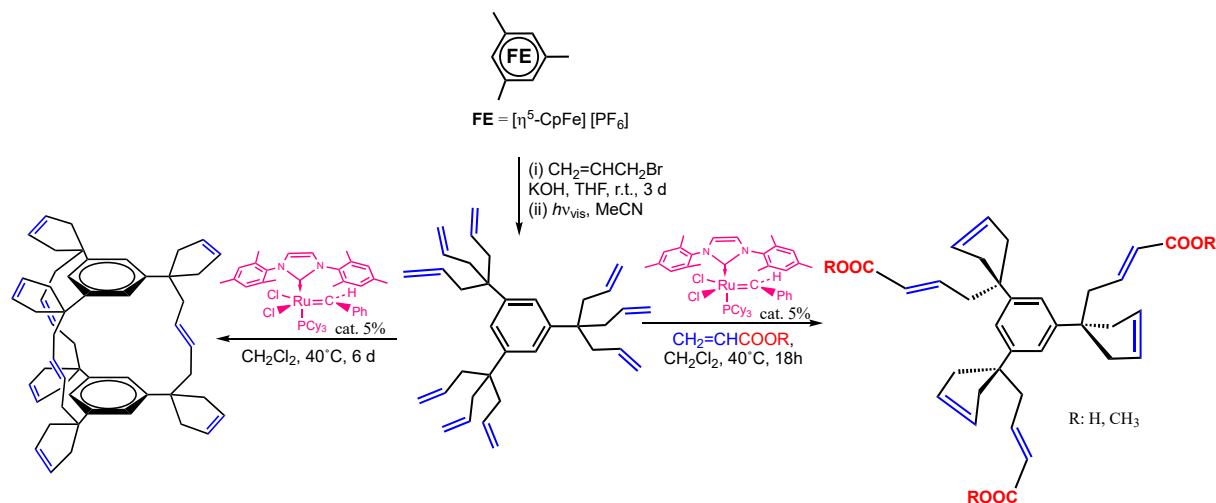
catalyst yielded a molecule with nine chloromethyl termini. Williamson reaction between the chloromethyl groups and the phenoltriallyl dendronic brick (also synthesized by  $\text{CpFe}^+$ -induced allylation) afforded the dendrimer of first generation with 27-allyl termini. The iteration of hydrosilylation and Williamson reaction was repeated until obtaining dendrimers of generation 9 with a theoretical number of more than 177 000 branches (Figure 5).<sup>54</sup> The completion of each reaction was followed by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR and the series of giant dendrimers were characterized by a variety of techniques such as size-exclusion chromatography (SEC), transmission electron microscopy (TEM) and AFM.



**Figure 5.** Divergent construction of a series of giant organic dendrimers using the nona-allyl core G<sup>0</sup>-9-allyl) and the phenoltriallyl dendronic brick (dendron A) built by  $\text{Cp-Fe}^+$ -induced allylation. a) Abbreviated dendrimer names upon growth by triple branching from the zeroth generation G<sup>0</sup>-9-allyl to the 9th generation (G<sup>9</sup>) dendrimer with a theoretical number of 177147 allyl termini; b) construction of the early (G<sup>0</sup> and G<sup>1</sup>) dendrimers represented in a) upon  $\text{CpFe}^+$ -induced tris-allylation of methyl groups of the arene ligands and subsequent functionalization towards dendrimers. The MALDI TOF mass spectrum (MS) showed that the molecular pic of the 2<sup>nd</sup> generation-81-allyl dendrimer obtained was almost pure. Larger generations showed major MS defects inherent to the divergent construction, although  $^1\text{H}$  and  $^{29}\text{Si}$  NMR allowed following the dendrimer construction until G<sup>9</sup>.<sup>54</sup>

This family of dendrimers is the largest reported so far, way beyond the dense-packing limit calculated by De Gennes for the PAMAM dendrimers. These giant dendrimers opened the door for the synthesis of giant molecular batteries and provided insights about the dynamics of the tridimensionality of dendrimers.<sup>54</sup>

The nona-allyl dendrimer core bearing nine terminal olefins<sup>52</sup> was a perfect target for olefin metathesis reactions.<sup>67</sup> The nona-allyl dendrimer in the presence of Grubbs catalyst of 2<sup>nd</sup> generation underwent ring-closing metathesis (RCM) privileging the formation of cyclopentenyl groups on the branches, a very fast reaction that is thermodynamically favored due to the resulting five-membered rings. The fate of the remaining third allyl branch was interesting to study. Intermolecular metathesis was much slower than the intramolecular RCM and led to various oligomers. Repeated use of mass spectrometry showed that the oligomeric mixture progressively converged to a cage compound, the thermodynamic product, resulting from three metathesis reactions of the three remaining allyl groups of two arene molecules (Scheme 7).<sup>67</sup> On the other hand, in the presence of an olefin with an electron withdrawing group (acrylic acid or methyl acrylate), Grubbs catalyst of 2<sup>nd</sup> generation still promoted the RCM yielding the cyclopentenyl groups, but the remaining allyl branch underwent cross metathesis (CM), leading to functionalization (Scheme 7).<sup>67-69</sup>

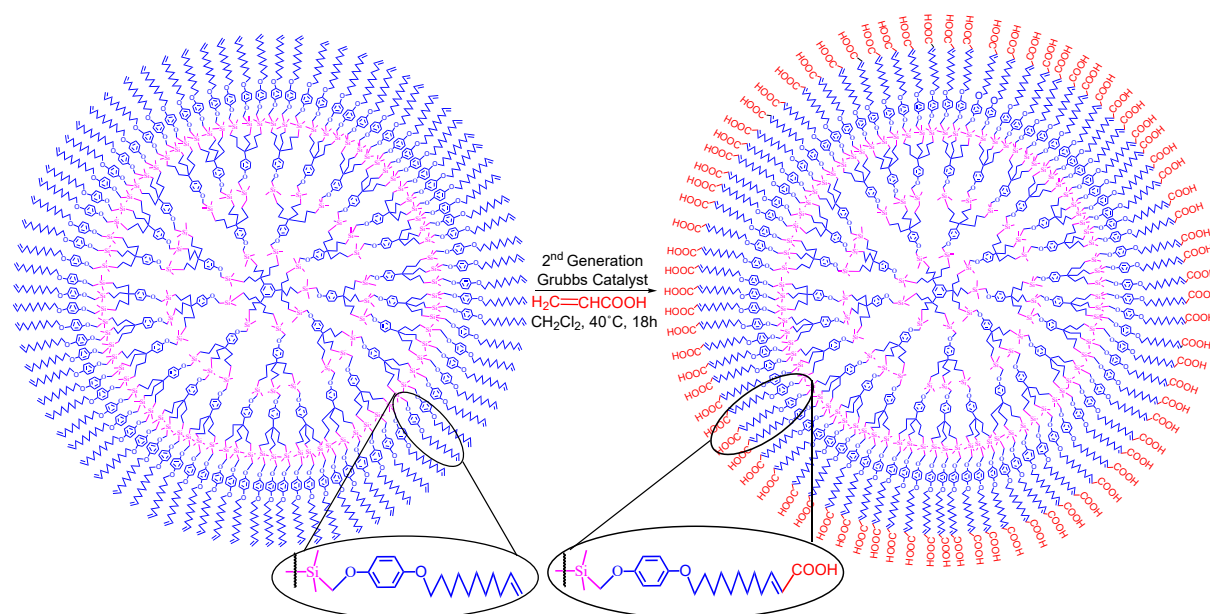


**Scheme 7.** Multiple metathesis reactions using Grubbs Catalyst of 2<sup>nd</sup> generation on a nona-allyl core: cage formation (left) vs. functionalization in the presence of a cross metathesis substrate (right). Adapted with permission from ref 68. Copyright 2003 Wiley-VCH.

The only way to avoid the RCM and formation of the cyclopentenyl groups was significantly lengthening the dendrimers' tethers precluding the formation of the five-membered rings. Indeed, such synthetic strategy allowed the full functionalization of



dendrimers with nine, twenty-seven and eighty-one termini through cross metathesis (CM).<sup>68,69</sup> This work from Didier's group paved the way to use CM as an efficient reaction to functionalize polyolefin dendrimers, polymers and metal nanoparticles with acrylic derivatives including acrylic acid (Scheme 8).<sup>69</sup>



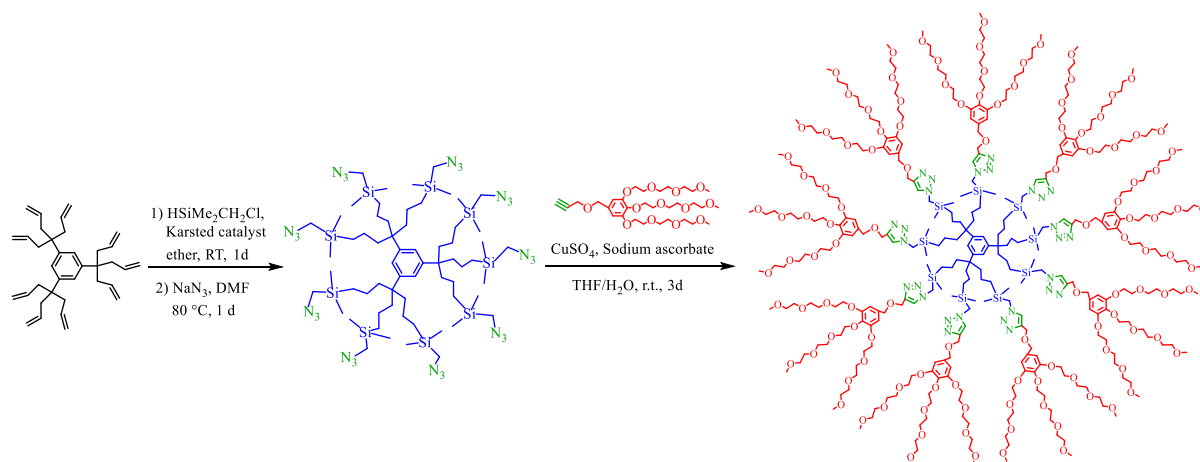
**Scheme 8.** Catalysis of cross olefin metathesis of a 81-allyl-terminated dendrimer with acrylic acid catalyzed by the 2<sup>nd</sup>-generation Grubbs catalyst [Ru(=CHPh)(bis-mesityl NHC)(Cl)<sub>2</sub>(PCy<sub>3</sub>)] yielding a 81-carboxylic acid-terminated dendrimer (flat representations of the dendrimers).

Ferrocenyl groups were also introduced at the termini of dendrimer tethers through CM, which was of interest, since such group have potential applications towards molecular electronics<sup>62,70</sup> and, recently, nanomedicine<sup>71</sup> including anticancer agents.<sup>71,72</sup>

Another noteworthy contribution of Didier's group to the use of metathesis reaction in dendrimer chemistry was the use of CM to build dendrimers.<sup>69</sup> A dendron containing an acrylic group at the focal point and three chloromethyl groups as branches, was used as the dendronic brick to construct a new series of dendrimers bearing internal olefins using an iteration of CM and Williamson reaction. This synthetic strategy was an ingenious way to grow dendrimers from a generation to the next<sup>69</sup> according to Newkome's 1 → 3 branching type.<sup>73</sup>

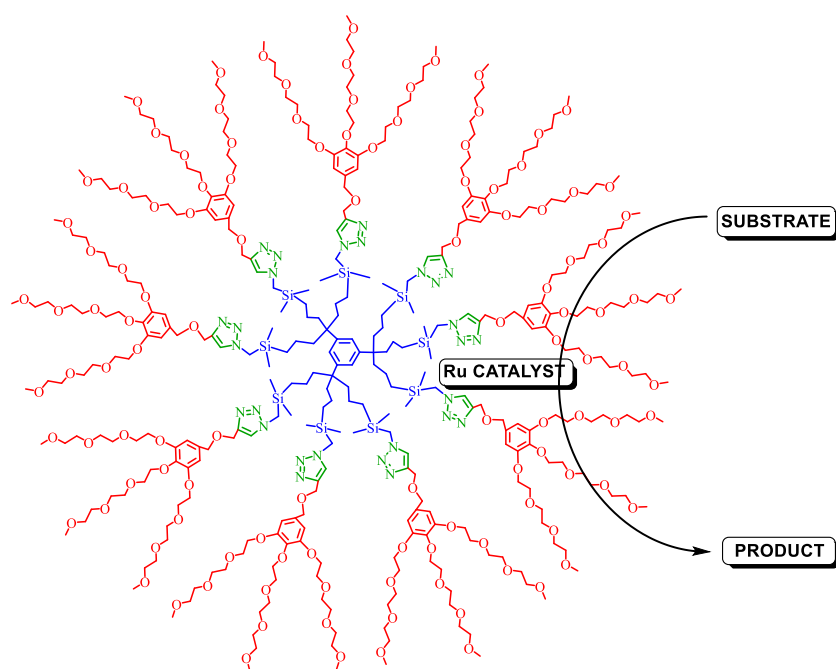
Another unique contribution of Didier's group in olefin metathesis catalysis was the use of dendrimers as molecular micelles to protect the catalyst and olefin substrates in the hydrophobic interior of amphiphilic dendrimers, in order to carry out olefin metathesis in water with high turnover numbers of the metathesis catalyst. Therefore, a 27-tri(ethylene glycol)-terminated amphiphilic dendrimer was synthesized by copper catalyzed azide alkyne cycloaddition

(CuAAC) “click” chemistry between a nonaazido dendrimer derived from the above nona-allyl dendrimer and a dendron containing a propargyl group at the focal point and three triethylene glycol branches (Scheme 9).<sup>74</sup>



**Scheme 9.** Synthesis of the standard 27-triethylene glycol dendritic nanoreactor often used in the Astruc group as a molecular micelle for various highly efficient catalytic reactions (flat representation of the dendrimers).

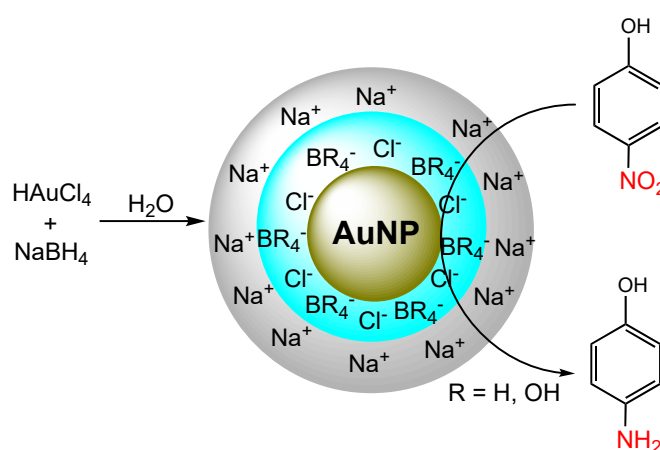
High to near-quantitative olefin metathesis yields were obtained in various RCM and CM reactions in water using only 0.1 mol % of the Grubbs catalyst of 2<sup>nd</sup> generation [Ru(=CHPh)(NHC)(Cl)<sub>2</sub>], (NHC = 4,5-dihydroimidazolin-2-ylidene) and 0.083 mol % of the dendrimer that could be recycled many times in water. On the other hand, under similar conditions, no metathesis product was obtained in the absence of the amphiphilic dendrimer. These results were enabled by the intradendritic protection of the metathesis catalyst. This ruthenium metathesis catalyst is stable in water, but not in the presence of a terminal olefin, presumably because the methylene species [Ru(=CH<sub>2</sub>)(NHC)(Cl)<sub>2</sub>] that are generated *in situ* upon one metathesis cycle with the terminal olefin is very reactive, suffering side reactions in water in the absence of this intradendritic protection (Figure 6).



**Figure 6.** Schematic principle of efficient catalyzed cross metathesis inside the micellar dendritic nanoreactor. The TEG periphery solubilizes the dendrimer in water, while the hydrophobic intradendritic core solubilizes the catalyst, substrate and product.

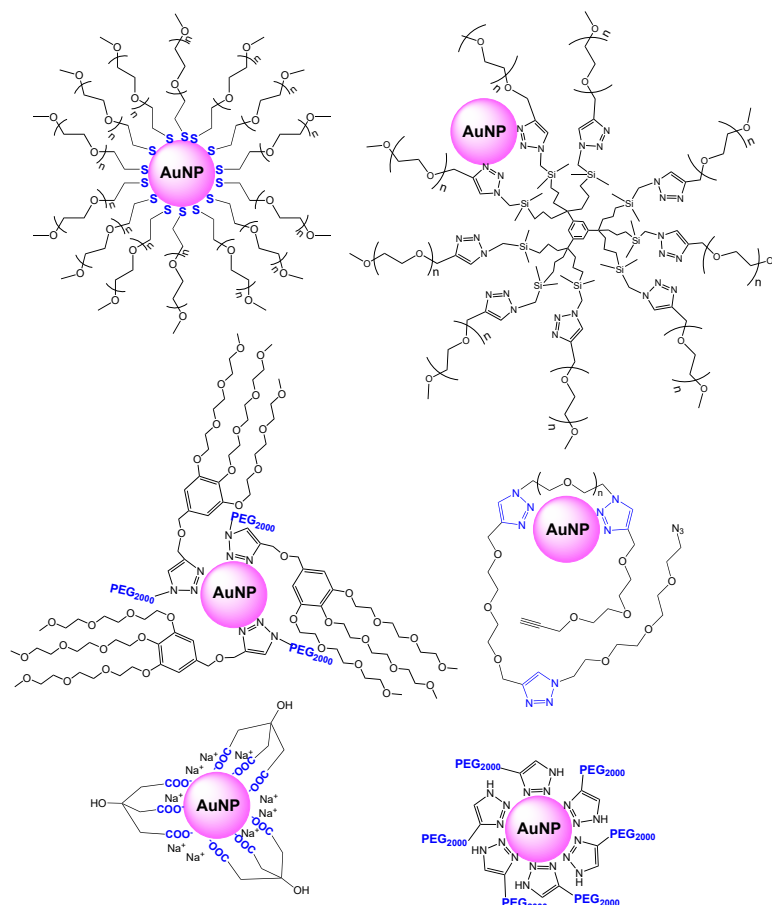
## NANOCATALYSIS

Dendrimers and nanoparticles have in common the nanosize, and their interplay involving various supramolecular interactions<sup>75</sup> was an inspiring concept for the Astruc group in catalysis in the 2000's.<sup>9</sup> A seminal report mixing star- or dendrimer-shaped nanoparticles was published then with Pd nanoparticle-centered frameworks, as it was realized that the thiolate ligands did not inhibit nanocatalysis of cross carbon-carbon coupling reactions.<sup>76</sup> Such nanoparticle-centered star-shaped frameworks,<sup>77</sup> dendrons<sup>78</sup> and dendrimers<sup>79</sup> were also extended to gold nanoparticles given their multiple interests and applications.<sup>80,81</sup> Blending nanoparticles and dendrimers towards catalysis was optimized in the Astruc group with the triazole-containing dendrimers<sup>82,83</sup> and extended to non-dendritic triazole-stabilized nanocatalysts.<sup>84</sup> Indeed, it was discovered that simple reduction with NaBH<sub>4</sub> of the nanogold precursor HAuCl<sub>4</sub> in water under ambient conditions, even in the absence of macromolecule, was sufficient to stabilize for more than one month a very efficient nanogold catalyst (3 nm) towards nitrophenol reduction to aminophenol (Scheme 10).<sup>85</sup> Borane hydrolysis provided electrostatic stabilization of the AuNP by Cl<sup>-</sup> and B(OH)<sub>4</sub><sup>-</sup> (as a mildly protecting metaborate hydrate polymer) near the AuNP core with their Na<sup>+</sup> cations standing behind (as shown in Scheme 10).



**Scheme 10.** Catalytically very efficient AuNPs synthesized simply from  $\text{HAuCl}_4$  and  $\text{NaBH}_4$  in water.

$\text{NaBH}_4$  is a very common reducing agent in organic and inorganic chemistry, and early on Didier's group had shown single-electron transfer mechanism with this reagent and its use as a single-electron transfer reagent.<sup>86</sup> This provided an opportunity to investigate the behavior of AuNPs as catalytically active electron reservoirs,<sup>87</sup> another property that metal NPs and redox robust metallodendrimers have in common.<sup>69,88</sup> AuNPs were indeed shown to be redox catalysts for which the stereoelectronic influence of the stabilizing ligands in catalyzed 4-NP reduction was crucial. The anionic thiolate ligands were much less efficient than neutral triazole-based ligands (Figure 7), possibly because of additional charges in AuNPs accumulated upon reduction with excess  $\text{NaBH}_4$  of the  $\text{HAuCl}_4$  precursor and the reduced electron density on the AuNP surface given the polarity of the Au-S bond.<sup>84,87</sup>

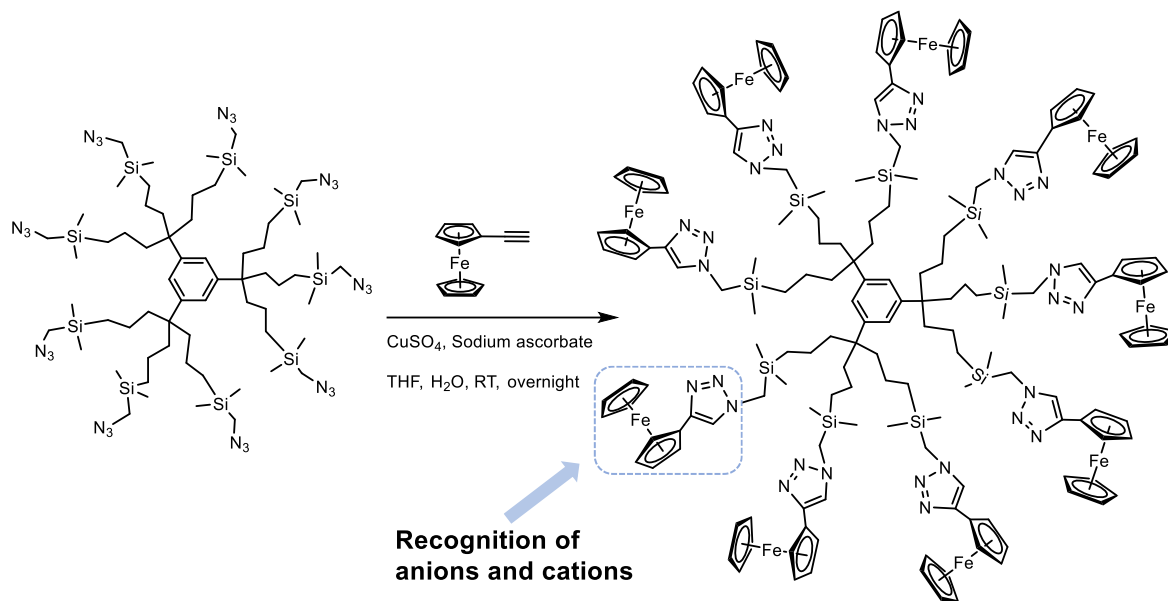


**Figure 7.** Various AuNP ligands compared for their stereo-electronic effects in the reduction of 4-nitrophenol.

## TRIAZOLE-CONTAINING DENDRIMERS AS TEMPLATES FOR NANOPARTICLE CATALYSTS

In the 2000's, Sharpless and co-workers defined the new concept of “click” Chemistry and the CuAAC reaction appeared as an amazing solution for many synthetic problems in organic chemistry and materials science.<sup>89</sup> Didier's group was among the first ones to apply this reaction to dendrimer science and, definitely, the first research group to synthesize metallodendrimers using CuAAC.<sup>90</sup> A new series of ferrocenyl dendrimers containing triazole groups in the interior dendrimer backbone was fully synthesized using CuAAC between azido-terminated dendrimers and a derivative of phenoltriallyl with a propargyl group at the focal point. The ferrocenyl groups were introduced at the dendrimer's periphery through CuAAC reaction between the azido-terminated dendrimers and ethynylferrocene (Scheme 11). This synthetic strategy was a landmark finding, not only due to the high yields and beauty of the new series of dendrimers created,<sup>90-100</sup> but mainly due to the many scientific outcomes that were generated through these dendrimers in the areas of redox sensing, nanoparticles' synthesis, catalysis, and

later on supramolecular vesosomes with non-traditional intrinsic luminescence (NTIL).<sup>72,82,90,101</sup>

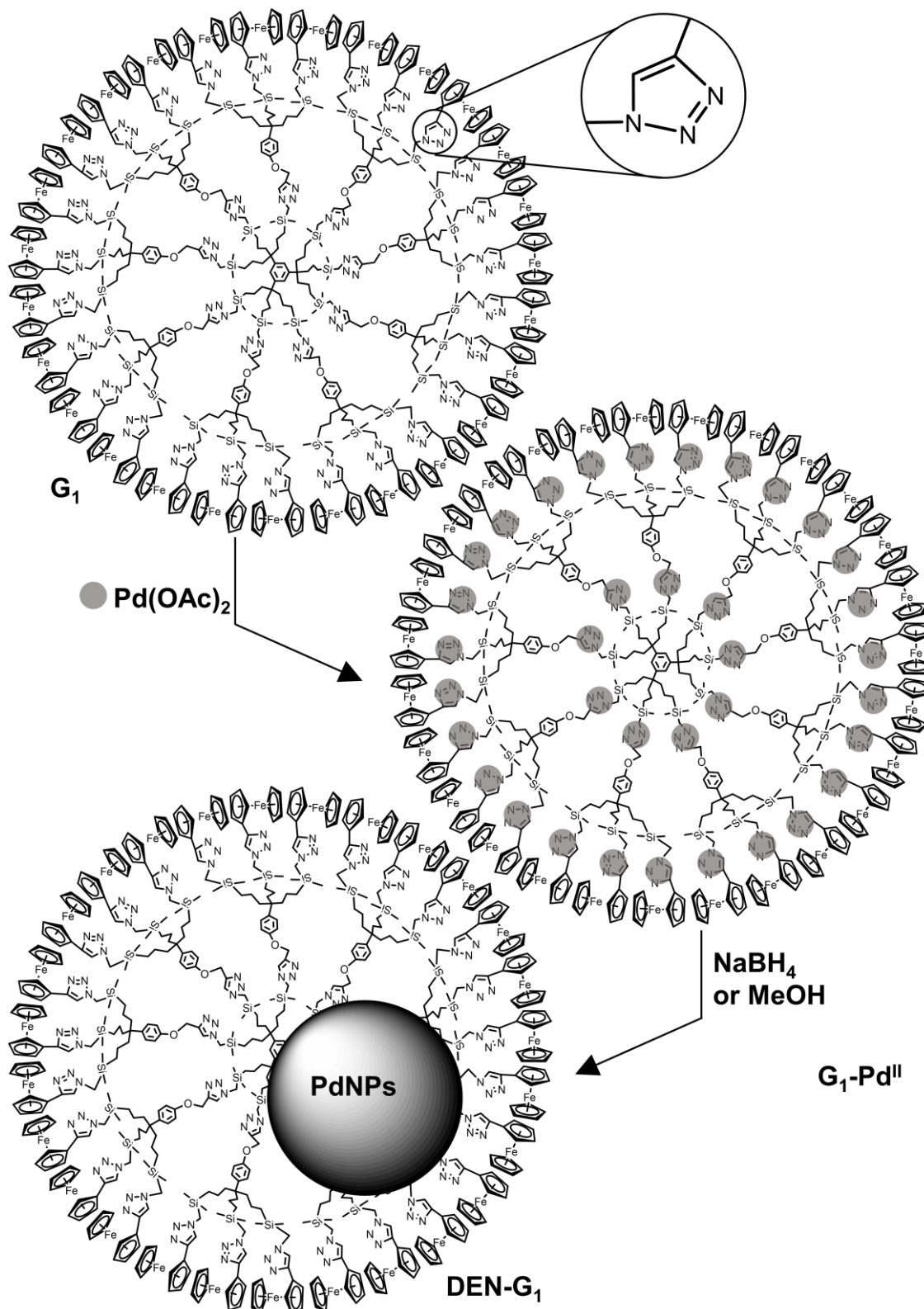


**Scheme 11.** Synthesis of the triazolylferrocenyl dendrimers through CuAAC reaction.

Indeed, the 1,2,3-triazolyl groups formed upon CuAAC “click” reaction of the dendrimer branches<sup>95</sup> are mild nitrogen ligands located inside dendrimers’ backbone between the very center and the periphery, and were used to explore the coordination of a variety of transition-metal ions.<sup>97-100</sup>

Taking advantage of the ferrocenyl group redox properties, the triazolylferrocenyl dendrimers were tested for molecular recognition, and it was found that they were able to sense both oxo anions and metal cations.<sup>90</sup> The triazole group adjacent to the ferrocenyl redox center coordinates to metal cations such as  $\text{Pd}^{2+}$ ,  $\text{Pt}^{2+}$ ,  $\text{Cu}^+$  and  $\text{Cu}^{2+}$ , and binds to oxoanions such as  $\text{ATP}^{2-}$  significantly changing the redox potential of the ferrocenyl dendrimer probe.<sup>90</sup> The coordination of metals inside the triazole-containing dendrimers was further explored by Didier’s group to produce ultra-small palladium nanoparticles with a precise number of metal atoms. Upon reduction of the Pd(II) coordinated to the triazole groups, the Pd(0) atoms leave the triazole ligands and agglomerate inside the dendrimers forming dendrimer encapsulated nanoparticles (DENs). In triazolylferrocenyl-terminated “click” dendrimers, the bulk ferrocenyl groups make a protecting wall at the dendrimer periphery preventing NP escape and agglomeration outside the metallodendrimers (Scheme 12). For the first and second dendrimer generations containing 27 resp. 81 branches, the sizes of the PdNPs measured by TEM fitted

the theoretical numbers calculated using one Pd atom *per* intradendritic triazolyl ligand (36 resp. 117 atoms). In the case of the 0<sup>th</sup>-generation dendrimer with only 9 branches, the dendrimer was too small to stabilize intradendritic palladium nanoparticles (PdNPs); therefore, larger PdNPs were then stabilized by several dendrimers at their periphery forming dendrimer-stabilized nanoparticles (DSN).<sup>90</sup> A similar situation was encountered in the absence of “click” triazolyl ligands on the branches.<sup>102</sup> Didier’s group has shown that the Pd DENs<sup>103</sup> prepared with “click” dendrimer templates were extremely active in catalysis for olefin hydrogenation and C-C cross coupling reactions.<sup>82,92</sup>

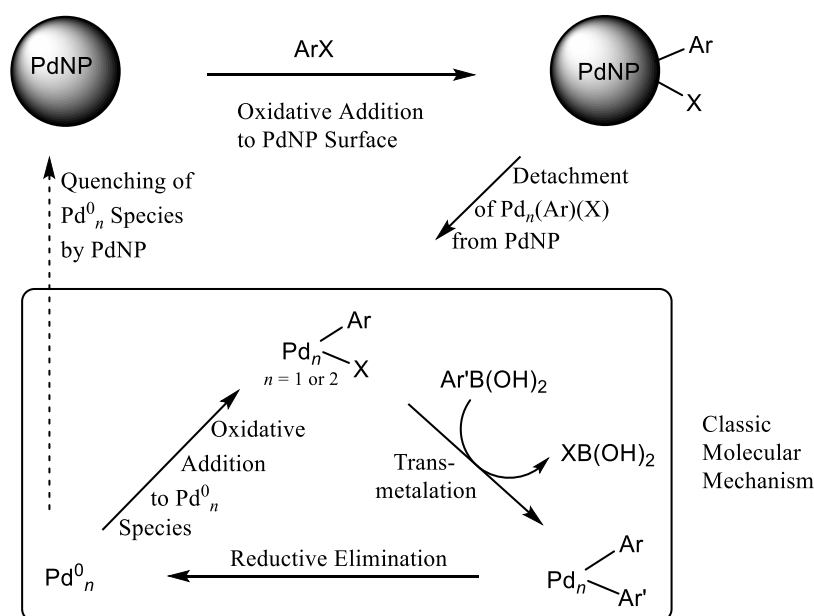


**Scheme 12.** Flat representation of 1<sup>st</sup>-generation of ferrocenyl-terminated click dendrimer that coordinates  $Pd^{II}$  on the triazole groups and encapsulate  $PdNPs$  for ppm catalysis of the Miyaura-Suzuki reaction. The number of Pd atoms in the  $PdNP$  (as for the 1<sup>st</sup>-dendrimer generation) represents (from the TEM size) one Pd atom *per* intradendritic triazole group.



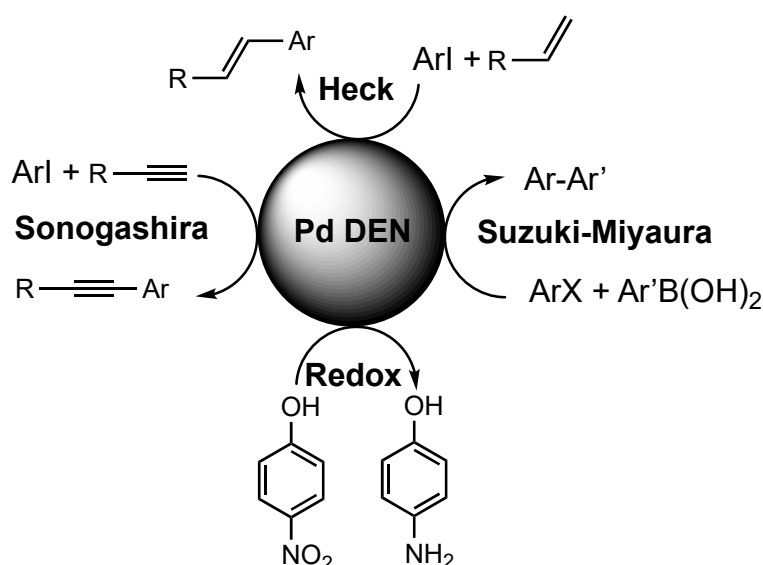
## “CLICK” DENDRIMER-SUPPORTED “SUB-PPM” NANOCATALYSIS

In PdNP-catalyzed Miyaura-Suzuki cross coupling between PhBr and PhB(OH)<sub>2</sub> utilizing the nona(ferrocenyltriazolyl)-terminated dendrimer as NP template under ambient conditions, reaction yields increased upon decreasing the nanocatalyst concentration. The turnover number (TON) reached 540 000 down to the ppm Pd level. It was proposed that Pd atom(s) leached from the PdNP, the leached Pd atom(s) being the active catalyst.<sup>82</sup> This behavior was taken into account by recombination of the Pd atoms all the less frequent as the Pd concentration decreased allowing, at low concentration, yield and TON increase upon concentration decrease. The Pd atom leaching mechanism was proposed for the C-C cross-coupling reactions with PdNPs by de Vries for Heck coupling reactions at 130°C (Scheme 13).<sup>104</sup> Didier’s work on the catalytic activity of the PdNPs stabilized by the triazolyl-ferrocenyl dendrimers demonstrated that the Pd atom leaching mechanism occurs at low temperature. In the proposed mechanism, the first step consists on the oxidative addition of the iodoaryl on the PdNP surface generating a Pd(II) atom that leaves the mother nanoparticle. This atom promotes the C-C coupling in solution and, through the reductive elimination step, it is reduced back to Pd(0), which can either be re-captured by the mother NP or start a new catalytic cycle. At higher concentration of NPs, the Pd(0) atoms are more easily captured by the mother PdNPs slowing down the catalysis; however, at very high dilutions the leached Pd(0) atoms rather engage in new catalytic cycles reaching higher TOFs and TONs (Scheme 13).



**Scheme 13.** Proposed leaching mechanism for the catalysis by extremely low amounts of Pd NPs for the Suzuki-Miyaura reaction between iodobenzene and phenyl boronic acid under ambient conditions. Reprinted from ref 79. Copyright 2007 Wiley-VCH.

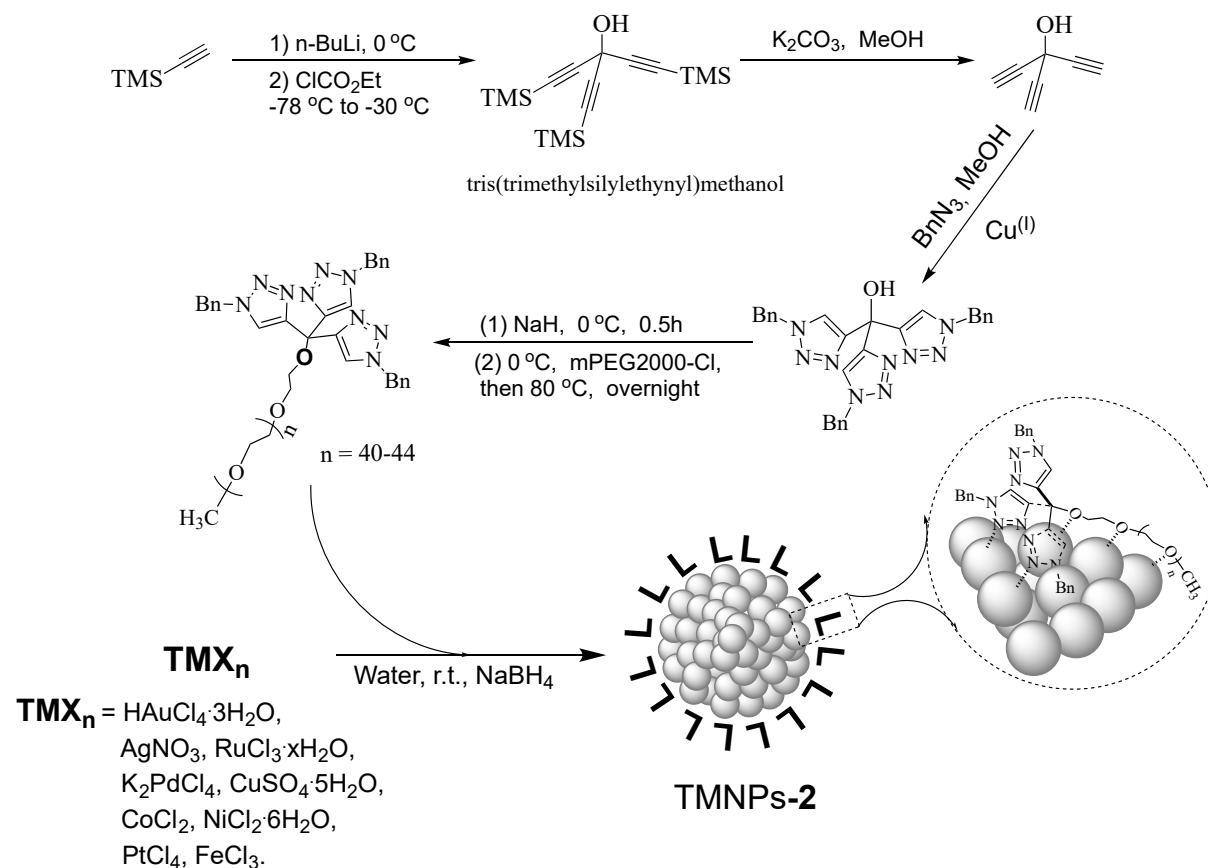
Didier's group translated these very good catalytic results to aqueous medium by synthesizing water-soluble triazolyl-containing dendrimers bearing sulfonate termini and triethylene glycol termini. The very small PdNPs encapsulated by the amphiphilic 27-triethylene glycol-terminated dendrimer (1 to 2 nm), were active in sub-ppm catalysis in aqueous solvents such as water:ethanol 1:1, for the Suzuki-Miyaura reaction between ArX and PhB(OH)<sub>2</sub> at 80°C for ArBr and 28°C for several ArI. With PhBr, using only 1 ppm Pd, 99% yield was obtained in the presence of 0.1% dendrimer, whereas no reaction occurred in the absence of this dendrimer. Such dendrimer-protected small PdNPs were also shown to be very efficient catalysts for other cross-coupling reactions (Sonogashira, Heck), nitrophenol reduction and olefin hydrogenation (Scheme 14).<sup>98,99,105-107</sup>



**Scheme 14.** Schematic representation of PdNPs encapsulated by a 27-triethylene glycol micellar dendrimer-active in ppm nanocatalysis for various cross C-C coupling and hydrogenation reactions.

Triazole ligands in redox active polymers were found to provide Pd and Au multifunctional nanomaterials as electrochrome, polyelectrolyte, sensor, electrode modifier, NP stabilizers and catalyst templates.<sup>95</sup> Recently, Didier's group interests also concentrated on NP catalysts based on earth-abundant metals and their optimization when compared to noble-metal nanocatalysts.<sup>90</sup> For instance, an amphiphilic tris(triazolyl)-polyethylene glycol (tris-trz-PEG) ligand, was designed for the synthesis of very small Fe, Co, Ni, Cu, Ru, Pd, Ag, Pt, and Au nanocatalysts, which were evaluated and compared for the model 4-nitrophenol reduction

reaction. Even earth-abundant nanoparticles proved to be efficient, although high catalytic efficiencies involving the use of only a few metal ppm of PdNPs, RuNPs, and CuNPs were shown to catalyze various reactions including Suzuki–Miyaura C–C coupling, transfer hydrogenation, and the CuAAC “click” reaction (Figure 8).<sup>98</sup>

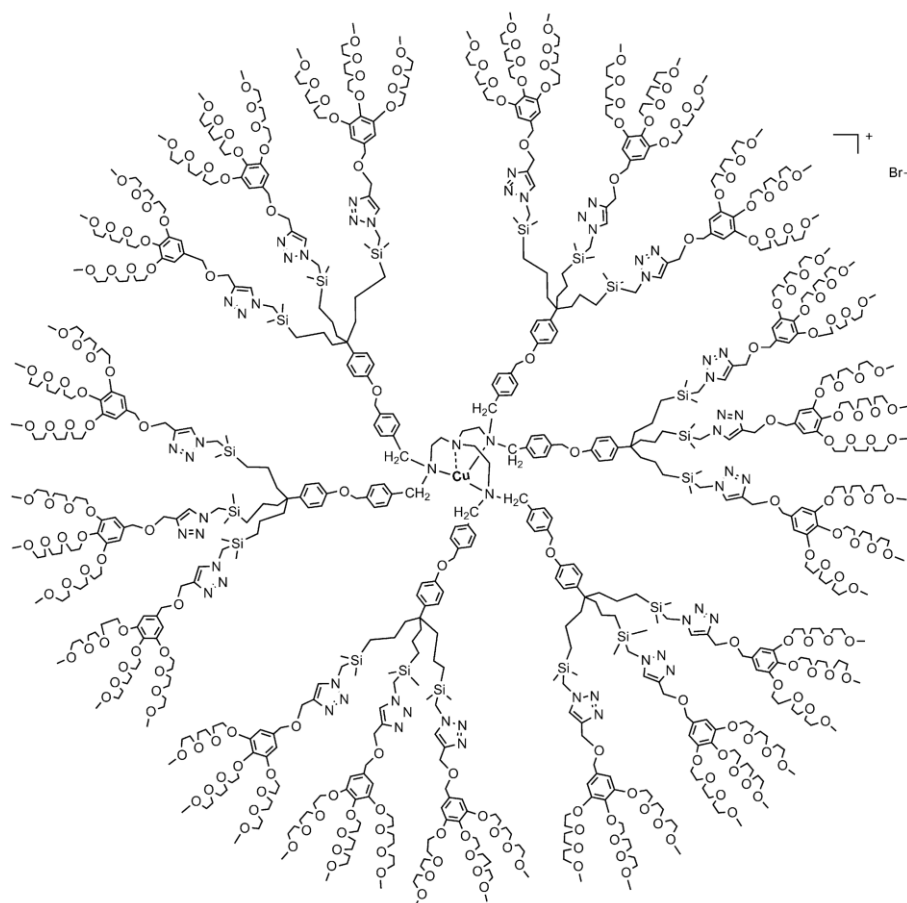


**Figure 8.** Synthesis of an amphiphilic ligand L = tris(triazolyl)-polyethylene glycol (tris-trz-PEG) and coordination of L to several late Transition Metal (TM) NPs for very efficient catalysis of various reactions ( $X_n$  = ligands in the precursor complex). Reproduced with permission from ref 98. Copyright 2016 Wiley-VCH.

In Didier’s group, metal NPs with “click” triazole-derived polymers<sup>93</sup> and dendrimers,<sup>94</sup> were sometimes found to form nanosnake-shaped AuNPs. For instance, upon designing dendrimer-stabilized nanocatalysts, AuNPs were all the better 4-nitrophenol reduction catalysts as they were less sterically inhibited by the dendrimer interior, whereas on the contrary CuNPs were all the better CuAAC “click” nanocatalysts as they are better protected from aerobic oxidation inside dendrimers.<sup>94</sup>

## CATALYSIS AND AUTOCATALYSIS OF THE CuAAC “CLICK” REACTION

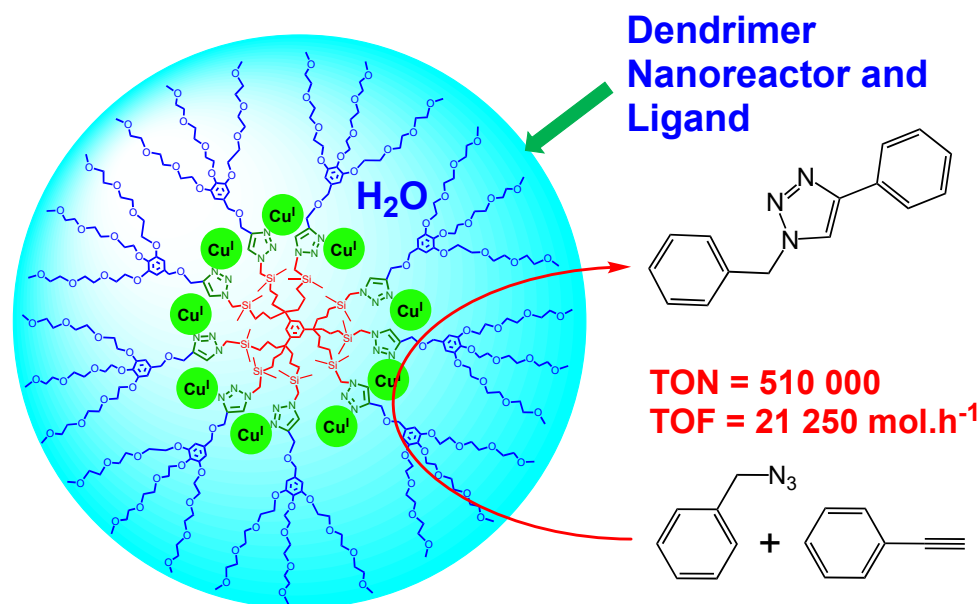
Sharpless' "click" concept is an extremely productive one in synthesis.<sup>89</sup> In CuAAC "click" catalysis, the most frequently used "click" reaction, the triazole-stabilized Cu(I) nanomaterial devices including metallamacromolecule ones, in particular by the Astruc group, were often found to be active catalysts (see the Nanocatalysis section). In these Cu nanocatalysts, XPS data showed that Cu was in the zero-oxidation state, although Cu(I) is known to be the catalytically active oxidation state in the CuAAC reaction. However, Cu(I) is easily generated *in situ* from the surface of Cu(0) nanomaterials, for instance upon reaction of the Cu surface with the terminal alkyne. Thus, molecular Cu(I) catalysts, especially tridentate-liganded ones, were optimized in Didier's group, such as those derived from the commercial ligand  $N(CH_2CH_2NH_2)_3$ , abbreviated tren.<sup>108</sup> It was developed in particular with  $(PhCH_2)_6tren$ , providing 100% yield of triazole in 10 min using 0.1 equiv. of recyclable Cu(I) catalyst with phenylacetylene and benzyl azide at room temperature. With Cu(I)-centered dendritic analogues containing 18 or 54 allyl or tri(ethylene glycol) branches (Figure 9), kinetic studies with small substrates showed even faster reactions than with  $(PhCH_2)_6tren$  indicating enzyme-like (nanozyme) behavior and demonstrating that a bimetallic mechanism would be sterically inhibited under these conditions.<sup>109</sup>



**Figure 9.** Flat representation of the Cu<sup>I</sup>(hexabenzyltren)-cored 54-TEG dendrimer, a water-soluble, relatively air stable, extremely active micellar nanozyme CuAAC click catalyst for the fast cycloaddition between benzyl azide and phenylacetylene. The parent catalyst Cu<sup>I</sup>(hexabenzyltren) itself also is a useful, although less fast, catalyst for this reaction. Reproduced with permission from ref 109. Copyright 2011 Wiley-VCH.

The second type of ligands examined in the Astruc group for catalysis of “click” reactions was the triethylene glycol tris(triazolate) ligand. A very good catalytic activity was obtained with a few ppm of Cu(I) catalyst that was applied to CuAAC reactions of a broad variety of substrates.<sup>110</sup>

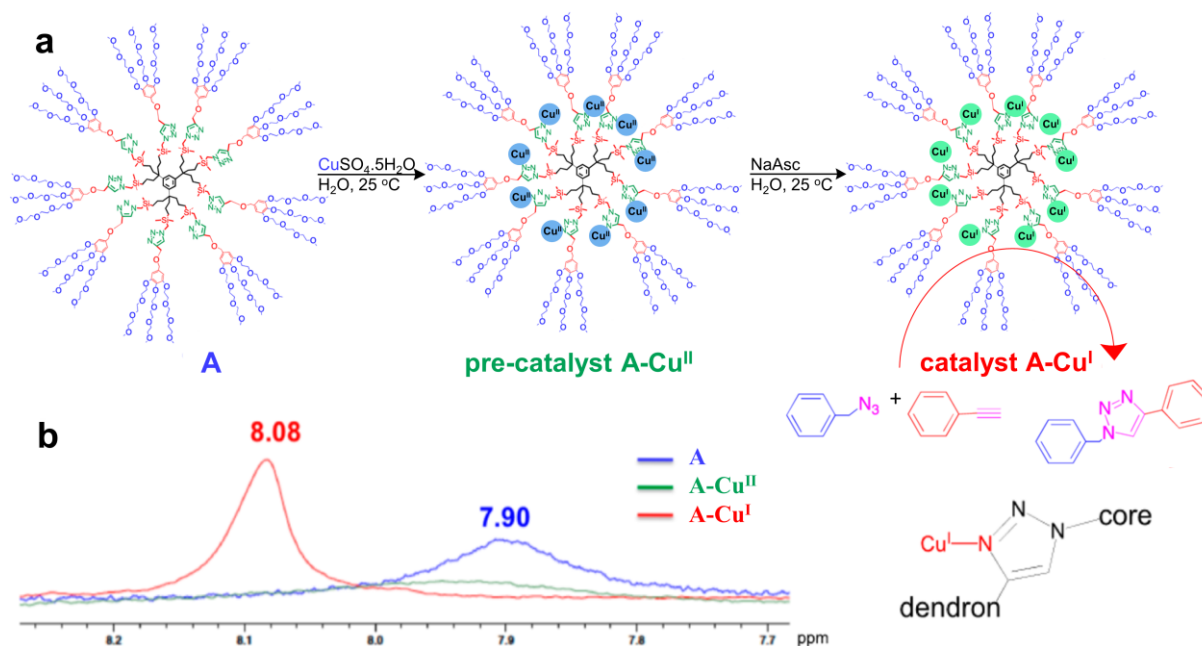
From the initial Sharpless catalyst of the CuAAC reaction using 10% of Cu(II) sulfate and sodium ascorbate, catalysts such as the above ones and many others in the literature have much improved the “click” reaction catalysis.<sup>83,111</sup> Another example indicated above with the toluene-soluble catalyst [(PhCH<sub>2</sub>)<sub>6</sub>tren]Cu(I)Br, provided a quantitative product yield at 25°C from phenylacetylene and benzyl azide with 0.1 mol % catalyst.<sup>109</sup> In water, however, the yield dropped to 2% due to solubility problems, and it was necessary to add 1 mol % of the (recoverable) unimolecular 27-triethylene glycol dendritic micelle serving as nanoreactor in order to recover a 91% yield (Figure 10).<sup>112</sup>



**Figure 10.** Schematic representation of the use of the 27-triethylene glycol dendritic nanoreactor for efficient catalysis using very low amounts of Cu(I) catalysts. Adapted with permission from ref 112. Copyright 2014 American Chemical Society.

This catalytic system was applied to a variety of substrates. The example of the reaction of the nona-azido dendritic core, the nanoreactor precursor, with the triethylene glycol dendron

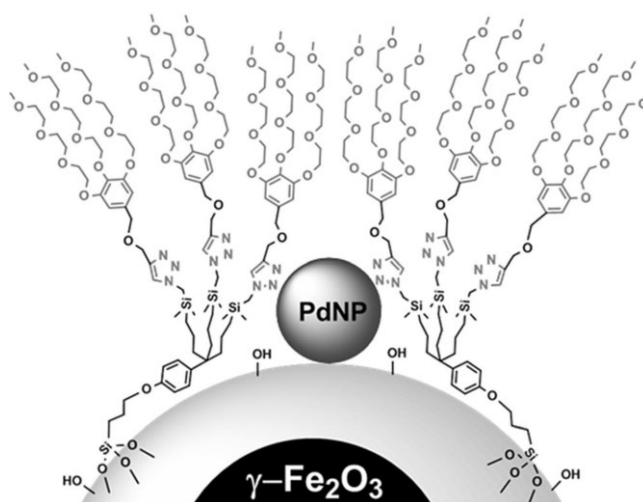
bearing a propargyl group in the apical position, was particularly interesting (Scheme 9). The "click" product was precisely that activating the "click" reaction leading to its own formation, i.e. the nanoreactor itself. This autocatalytic mechanism was proven by a strong acceleration of the reaction in the presence of 1 mol % of the final nanoreactor at the beginning of the reaction, the yield being more than double. The kinetic study showed that the conversion of the starting material after 90 min was already  $46 \pm 0.5$  % in the presence of 1 mol % of the nanoreactor against only 2 % without it at the beginning of the reaction. These experiments showed the marked micellar effect of the nanoreactor. Autocatalytic reactions have a particular significance, because such an autocatalytic mechanism appeared to be at the origin of life.<sup>113</sup> A practical improvement solution for the CuAAC "click" reaction was discovered in the Didier's group by simply utilizing in water the Sharpless catalyst to which 1 mol % of the nanoreactor was added. This strategy used the intradendritic triazole coordination and activation of Cu(I) that was proven *inter alia* by the downfield shift of the triazole proton on the <sup>1</sup>H NMR spectrum. Under these conditions, only 4 ppm Cu was necessary to obtain a quantitative yield of "click" product upon reacting phenylacetylene with benzyl azide (Figure 11). The performance was much weaker if the nanoreactor did not contain a triazole ligand, showing the cumulative accelerating effects of the micellar effect and intradendritic Cu(I) activation.<sup>112</sup>



**Figure 11.** a) 27-Triethylene glycol dendritic nanoreactor/ligand for CuAAC “click” catalysis. b) Comparison of the NMR signals of the triazole proton of the nanoreactor alone (7.90 ppm), with Cu(II) (very broad due to the paramagnetism) and Cu(I) (shift to 8.08 ppm) showing the coordination of Cu(I) to the nanoreactor intradendritic triazole. Reprinted with permission from ref 112. Copyright 2014 American Chemical Society.

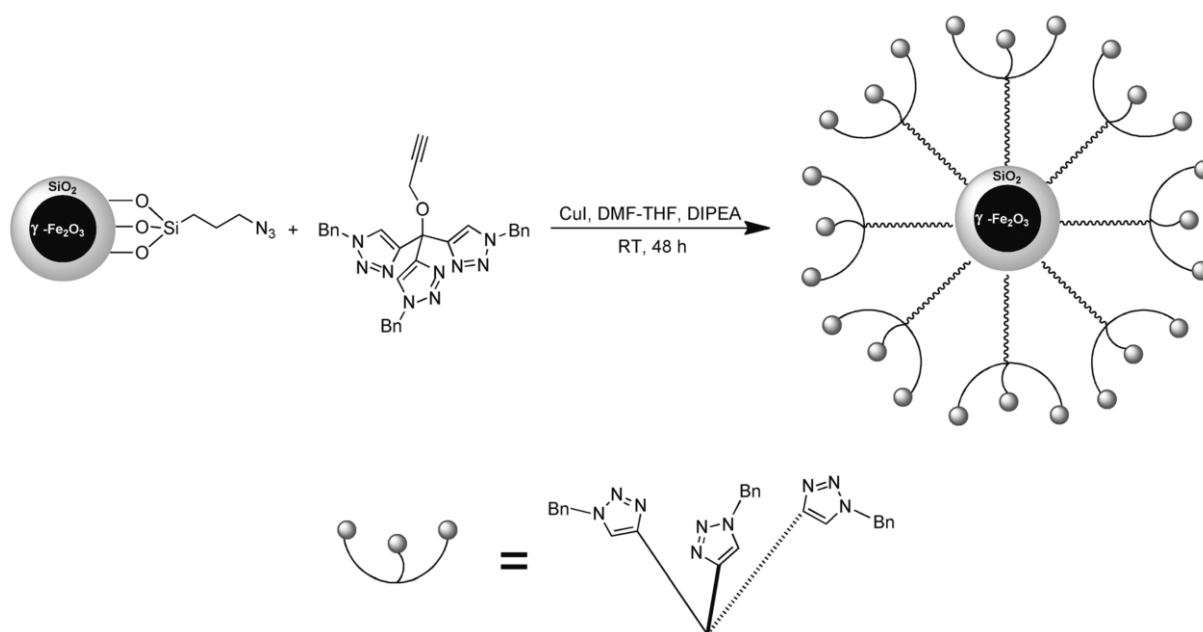
## MAGNETIC NANOCATALYSTS

Until the first decade of this century, Astruc's research had concentrated on homogeneous and semi-heterogeneous (NP) catalysis. For semi-heterogeneous NP catalysts (nanocatalysts), their large surface-to-volume ratio made them attractive alternatives to conventional catalysts, including substantial advantages in catalytic activity, selectivity, and stability. The use of magnetic nanoparticles (MNPs) was a solution of choice to benefit from these advantages of semi-heterogeneous NP catalysts and facilitate heterogeneous catalyst isolation and recycling. The area has been largely developed,<sup>114</sup> and the Astruc group has taken the opportunity of the triazole-containing macromolecular catalysts to blend them with a magnetic component in order to improve the green catalysis aspect.<sup>115</sup> Thus, magnetically recyclable PdNPs stabilized by “click” dendrimers were elaborated for C-C cross coupling and benzyl alcohol oxidation. Two synthetic strategies were used by Didier and his group, (i) a classic strategy involving the synthesis of a magnetic NP-ligand device followed by coordination with Pd(II) and reduction to Pd(0) NPs, and (ii) impregnation of a pre-synthesized macromolecule-stabilized PdNPs on magnetic NPs. With the first strategy, the best results in terms of Pd loading, reaction yields, recovery and recyclability were obtained, when the tethers were dendronic for supported magnetic PdNP-catalyzed cross C-C coupling reactions (Suzuki-Miyaura, Sonogashira and Heck reactions). Useful molecules including Felbinac, modified coumarines, cinamate derivatives and methyl cafeate were synthesized in high yields using these fully recyclable catalysts (Figure 12).<sup>116</sup>



**Figure 12.** Schematic representation of the engineered recyclable PdNP catalysts embedded inside the dendritic magnetic support towards various reactions. Reproduced with permission from ref 116. Copyright 2015 Wiley-VCH.

Another successful catalyst was obtained with a variation of this method upon branching of the tris(triazolate) ligand-terminated tether onto Pd yielding dendritic magnetic catalysts with  $\text{Fe}_2\text{O}_3@\text{SiO}_2$  NP at the core and the Pd(0) catalyst at the periphery (Figure 13) for efficient and selective benzyl alcohol oxidation to benzaldehyde with air.<sup>117</sup>



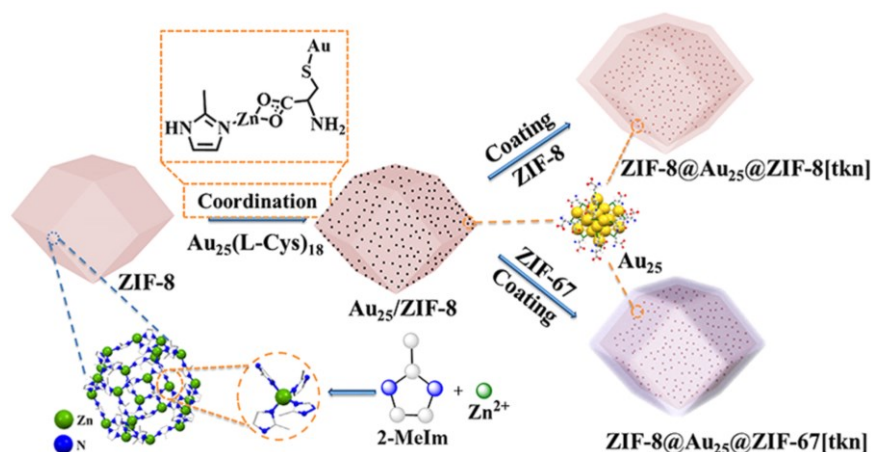
**Figure 13.** Synthesis of an efficient recyclable selective alcohol oxidation Pd catalysts coordinated to a tris(triazolyl) fragment branched to  $\text{SiO}_2@\gamma\text{Fe}_2\text{O}_3$  nanoparticles. Reproduced with permission from ref 117. Copyright 2015 Wiley-VCH.



Alternatively, in the impregnation strategy, the 1.4 nm PdNPs encapsulated in the 27-triethylene glycol dendrimer were ultrasonicated with the magnetic NP Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> to provide a fully recyclable magnetic catalyst that was active for quantitative and selective Miyaura-Suzuki coupling of phenylboronic acid with bromoarenes and benzylic alcohol oxidation with O<sub>2</sub>.<sup>118</sup> Interestingly,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs supported graphene oxide were found themselves to be excellent catalysts, even at the ppm level, for Suzuki-Miyaura coupling reactions and 4-nitrophenol reduction in aqueous solution.<sup>119</sup>

## NANOCLUSTERS IN CATALYSIS

Since their comprehensive review on gold nanoparticles and clusters in 2004,<sup>80</sup> Didier and his group have kept a great interest in late transition metal clusters,<sup>60,120-123</sup> and in particular on gold and other coinage metal clusters.<sup>81,85,118</sup> Indeed, catalysis by atomically-precise clusters are a rather new and very active sub-field of catalysis.<sup>123</sup> Recently, Didier and his co-workers compared the catalytic activity in CuAAC “click” reactions of several well-defined copper clusters, and it was found that the hexanuclear cluster [Cu<sub>6</sub>(C<sub>7</sub>H<sub>4</sub>NOS)<sub>6</sub>][Na<sup>+</sup>, THF] (C<sub>7</sub>H<sub>4</sub>NOS = 1,3-benzothiazol-2-olate) was by far the best Cu cluster catalyst owing to its thermal stability.<sup>124</sup> Didier Astruc also developed a collaboration with Manzhou Zhu's group at the University of Anhui in Hefei on the family of the representative Au<sub>25</sub>-thiolate and other clusters.<sup>24</sup> For instance Au<sub>25</sub>(L-Cys)<sub>18</sub> (Cys = cysteinyl) with terminal ligand groups COOH was sandwiched between the Zeolitic Imidazolate Frameworks ZIF-8 core and ZIF-67 at the periphery via Co<sup>2+</sup> coordination of peripheral carboxylate groups followed by addition of solution of 2-MeIm to form the outer ZIF-67 framework part. It was discovered that this precise robust composite nanosystem was an excellent catalyst for both nitrophenol reduction and carboxylation of terminal alkynes (Figure 14).<sup>125</sup>



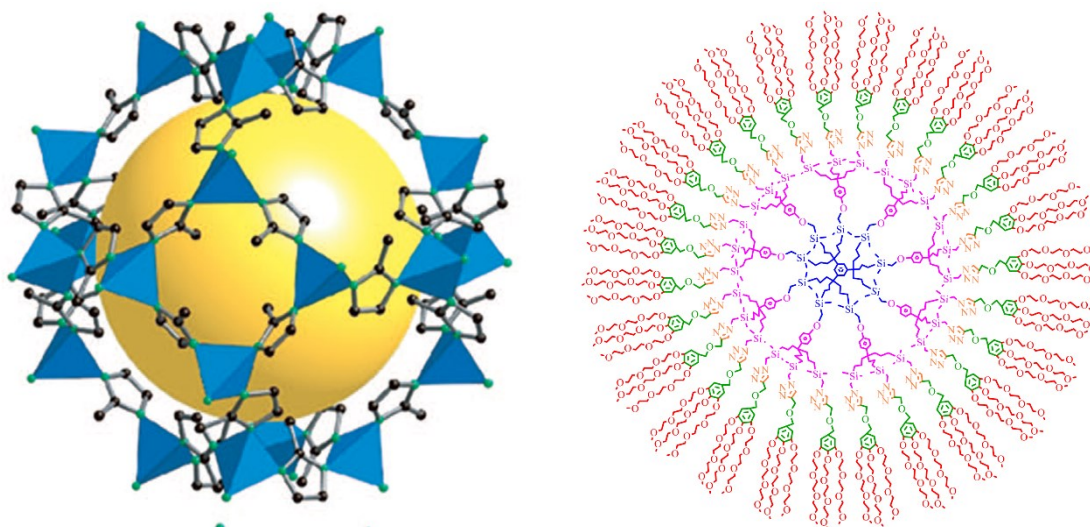
**Figure 14.** Schematic representation of the synthesis of the sandwich structures  $\text{ZIF-8@Au}_{25}@\text{ZIF-67}$  and  $\text{ZIF-8@Au}_{25}@\text{ZIF-8}$  (tkn is the shell thickness). Reprinted with permission from ref 125. Copyright 2020 American Chemical Society.

In another example, the coinage metal clusters  $\text{M}_1\text{Ag}_{21}(\text{dppf})_3(\text{SAdm})_{12}/\text{C}$  containing a mixture of 1-adamantanethiolate (SAdm) and 1,1'-bis-(diphenylphosphino)-ferrocene (dppf) nanoclusters supported on activated carbon (C) were proven to be efficient oxygen reduction reaction (ORR) catalysts in alkaline solutions, with  $\text{M}_1 = \text{Au}$  showing a better activity than  $\text{M}_1 = \text{Ag}$ , i. e. the Au atom boosted the catalytic activity of the all-Ag cluster.<sup>126</sup> Engineering modifications of the ZIF-8 framework can also considerably enhance the catalytic activity.<sup>127</sup> The isolation of precise atom clusters is sometimes of great mechanistic interest. A mixed coinage metal cluster  $\text{Au}_4\text{Cu}_4$  was found to capture a key intermediate,  $\text{Au}_4\text{Cu}_4-\pi$ -alkyne, of the CuAAC “click” reaction without alkyne deprotonation to a  $\sigma, \pi$ -alkynyl intermediate despite the common belief according which the alkyne would be deprotonated first before undergoing the CuAAC reaction.<sup>128</sup> Didier had already extended the function of electron reservoirs in redox catalysis to Au and PdNPs<sup>85,87</sup> and, given the crucial role of electron transfer in cluster catalysis, he recently examined this role with late transition-metal atomically-precise clusters.<sup>129</sup>

## HYDROGEN PRODUCTION

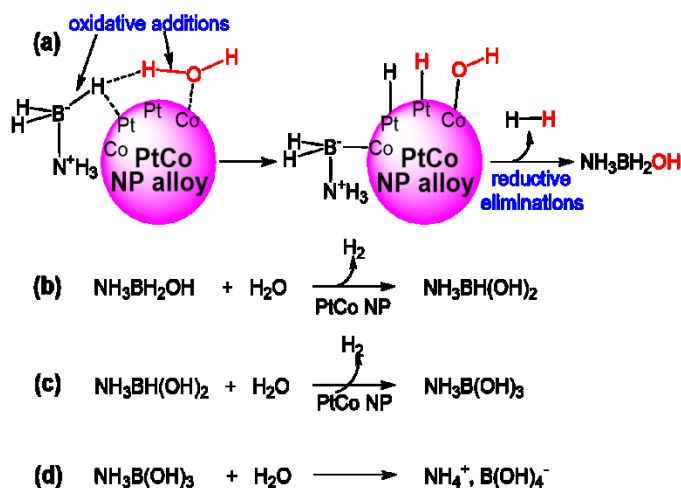
Sub-nanosized clusters inserted into dendrimers have been shown to be efficient catalysts for energy-related applications.<sup>130</sup> The active search for new carbon-free sustainable energy very recently led Didier to envisage new supports for the catalytic generation of hydrogen ( $\text{H}_2$ ) from hydrogen atom-rich precursors including water, ammonia borane, hydrazine borane, formic

acid/ sodium formate, sodium borohydride, tetrahydroxydiboron, and tetramethyldisiloxane.<sup>131</sup> All these H<sub>2</sub> precursors have been or are currently under study in the Astruc group. Research initially focused on the hydrolysis of ammonia borane and sodium borohydride, whereby nanocatalysis produces H<sub>2</sub> in which one hydrogen atom is provided by water and the other by the borane moiety.<sup>132</sup> Two types of supports were considered: (i) micellar dendritic nanoreactors (exo-receptors) in which the “click” dendrimer was terminated by 27 or 81 triethylene glycol groups that were already successfully used in nanocatalysis of “click”, C-C bond forming and oxidation reactions,<sup>83</sup> and (ii) zeolitic imidazolate frameworks (endo-receptors),<sup>133</sup> in particular ZIF-8 that has proved particularly efficient as MOF nanocatalysis nanoreactor (Figure 15).<sup>134</sup>



**Figure 15.** Endoreceptor (ZIF-8, left)<sup>133</sup> and exo-receptor (81-TEG dendrimer, right) nanoreactors used in the Astruc group as supports for nanocatalysis of H<sub>2</sub> generation from hydrogen-rich substrates. Reprinted with permission from ref 133 and 83, respectively. Copyright 2006 New York Academy of Science and 2012 American Chemical Society, respectively.

With “click” dendrimer nanoreactor supports, a dramatic synergy between Co and Pt in CoPt alloys was disclosed,<sup>135</sup> whereas with the ZIF-8 support, the best synergy in alloys shown to be located inside the ZIF-8 cavity was found between Ni and Pt (Figure 16).<sup>136</sup> With monometallic Ni NPs inside ZIF-8, the catalytic efficiency had been found to be remarkably efficient with this earth-abundant metal catalyst and, upon alloying Ni with Pt, not only a positive volcano-type nanocatalysis was obtained, but the best efficiency was found with only 1/3 Pt in the alloy.<sup>137</sup>



**Figure 16.** Proposed mechanism for the efficient alloyed MPt-nanocatalyzed (M = Co or Ni) H<sub>2</sub> production from ammonia borane hydrolysis under ambient conditions, the nanocatalyst support being either the ZIF-8 endoreceptor or a 27- or 81-triethylene glycol terminated dendritic exoreceptor. (a) substrates oxidative addition followed by products reductive elimination; (b) production of the 2<sup>nd</sup> H<sub>2</sub> molecule upon steps similar to (a); (c) production of the 3<sup>rd</sup> H<sub>2</sub> molecule upon steps similar to (a); (d) formation of ammonium tetrahydroxyborate.

This catalytic activity was controlled by acid-base equilibrium, i.e. it was enhanced by base and stopped by acid, so that H<sub>2</sub> was delivered on command from its precursor.<sup>136,137</sup> The presence of a plasmonic metal in the alloyed nanocomposite is known to induce visible-light acceleration of some reactions.<sup>129,138</sup> Although Au did not catalyze ammonia borane or sodium borohydride hydrolysis, alloying Au with a late transition metal sometimes favored the reaction, but strong positive effects were obtained in the presence of visible light that boosted the reaction because of the hot electron transfer generated in the fs time scale from plasmonic Au to the active metal-substrate site of the transition-metal catalyst.<sup>139</sup> In most of these systems, hydrogen production was used *in situ* for alkene hydrogenation with the same nanocatalyst (one pot) or Pd/C, a process that had been shown by the Astruc group early on to proceed stepwise (one H atom after the other).<sup>140-143</sup>

## CONCLUSION

Didier Astruc's career has grown from electron transfer catalysis, in connection with his concept of electron reservoirs in 1979,<sup>1,37,142</sup> to molecular and macromolecular catalysis around the turn of the century and during its first decade,<sup>143</sup> then to supramolecular nanocatalysis since 2007 after his disclosure and use of the first “click” metallodendrimers.<sup>82,90</sup> During the last few years,

the research of Didier Astruc and his group have compared exo-receptors and endo-receptors focusing mainly on energy-related aspects, in particular nanocatalysis for H<sub>2</sub> production<sup>131,132</sup> and CO<sub>2</sub> utilization,<sup>125</sup> including the use of visible-light illumination.<sup>139</sup> Didier Astruc's research has often combined nanocatalysis with original and very efficient dendritic construction following his seminal molecular bursting polyfunctionalization of  $\pi$ -complexes of aromatic compounds.<sup>52</sup> This spectacular incursion into macromolecular chemistry has not only allowed him to develop catalysis at the nano- and supramolecular level,<sup>82,112,135</sup> but also connect his catalytic interest to some other aspects such as multi-electron transfer,<sup>68,144</sup> electronic communication,<sup>145-147</sup> mixed valences,<sup>146</sup> batteries,<sup>70,148</sup> fluxionality,<sup>149</sup> gold nanodevices,<sup>79-81,83-85,87,137,150</sup> poly-ynes,<sup>151,152</sup> capsules,<sup>67,68</sup> electrostatic effects,<sup>153</sup> nanomedicine,<sup>72,154,155</sup> and redox sensors.<sup>156,157</sup> Didier has benefitted in France from the examples of his elder colleagues Henri Kagan,<sup>113,158</sup> John Osborn,<sup>159</sup> Yves Chauvin<sup>42</sup> and Jean-Marie Basset<sup>160</sup> in catalysis, Jean-Marie Lehn<sup>75,161</sup> and Jean-Pierre Sauvage<sup>161,162</sup> in supramolecular chemistry and catalysis, Bianka Tchoubar<sup>21,22</sup> in molecular mechanisms, and internationally of interactions with many others scientists cited in this Account. It was a pleasure to share some of Didier's ventures and now to revisit here his exceptional scientific career. We are incredibly grateful and privileged for having worked with an outstanding scientist, and we wish him many more great accomplishments.

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