

## One-pot multiple C-C bond formations toward dendrimers

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This Review article is dedicated to our distinguished colleague and friend Professor Léon Ghosez on the occasion of this Commemorative Issue

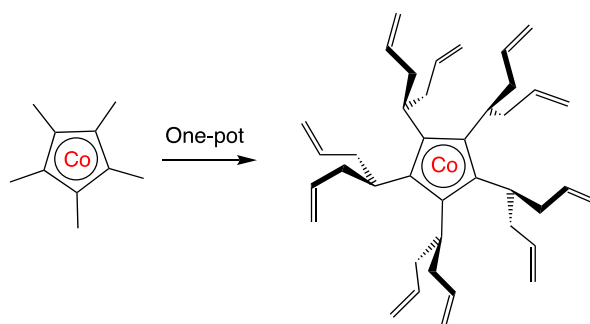
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### Abstract

This Account proposes comments on one-pot multiple carbon-carbon bond formation reactions based on literature and experience acquired in our laboratories during the last decades. In the late 1970s, our group disclosed the iron-induced one-pot multiple C-C bond formation in arene chemistry that was later developed toward dendrimer constructions. Here, we start by comparing one-pot multiple C-C or C-N bond in macromolecules including dendrimers, polymers, and gold nanoparticles. Then, we move from multiple C-C bond formation in the form of AAAA... processes to the one-pot metal-induced multiple C-C bond formation by ABABABAB... processes developed in our groups, including triple branching construction of dendrimers pioneered by Newkome *et al.*



**Keywords:** One-pot chemistry, multiple carbon-carbon bond formation, dendrimer, dendrimer core, metal-induced arene activation, sandwich complexes

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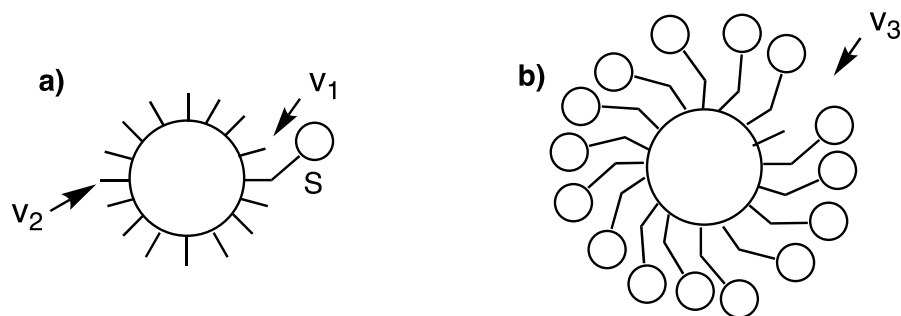
## 1. Introduction

Upon dedicating a mini-review article in honor of Professor Léon Ghosez, whose career<sup>1</sup> was much influenced by his mentor Robert B Woodward,<sup>2</sup> we propose to briefly comment on late-transition-metal-induced one-pot multiple C-C and other C-element bond-formation reactions, in particular toward branched nano- and dendritic structures. The relatively recent advent of metal-organic frameworks (MOFs)<sup>3</sup> offered new opportunities to catalyze tandem reactions by transition-metal moieties.<sup>4</sup> However, there has already been considerable know-how of tandem reactions in natural product synthesis<sup>5</sup>, including biomimetic synthesis<sup>6</sup> and, in such reactions, transition-metal homogeneous<sup>7</sup> and heterogeneous<sup>8</sup> catalysis play key roles. More recently, transition-metal-catalyzed tandem reactions have proven useful for CO<sub>2</sub> reduction.<sup>9</sup>

Here, some comments are suggested concerning multiple one-pot C-C and other C-element bond-formation reactions upon nano- and dendritic-material constructions, a field pioneered by Tomalia *et al.* with C-N bond formation and Newkome *et al.* with C-C bond formation in the early 1980s,<sup>10-12</sup> with, later, notable applications in *inter alia* biomedicine,<sup>13,14</sup> materials science<sup>15,16</sup> and catalysis.<sup>17,18</sup>

## 2. The Problem of Dendrimer Purity

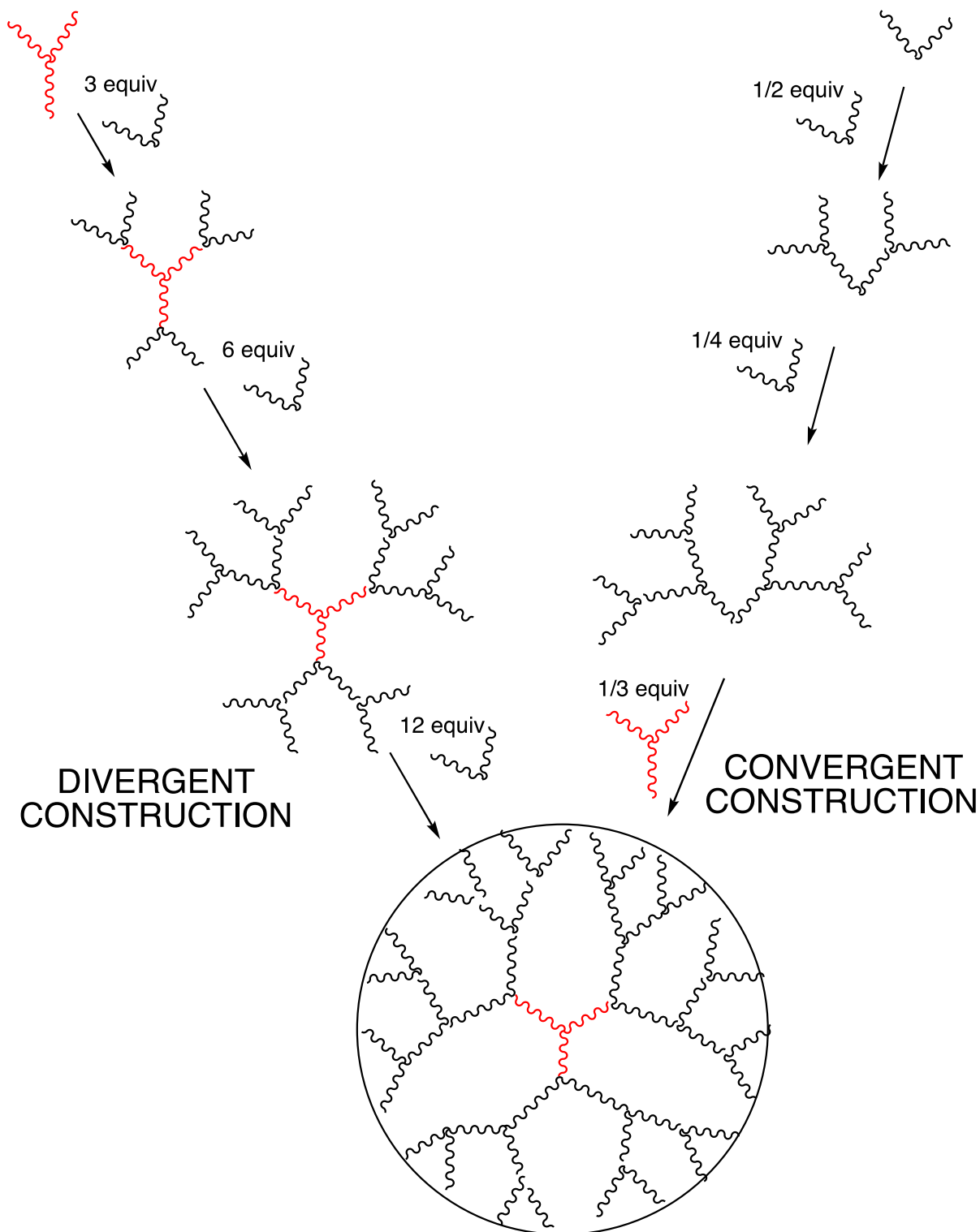
In divergent dendrimer construction, from one generation to the next one, a given reaction is applied to all the dendrimer branches, i.e., one is dealing, for instance, with one-pot successive C-C or C-element bond-formation reactions. However, in such dendrimer chemistry, although all the reactions on the different branches look identical, they are not exactly so because the microenvironment of the reaction changes from one branch to the next. The difference of microenvironment is minute if the reaction on the next tether occurs far from the preceding one, however, the microenvironment progressively undergoes major stereoelectronic changes, influencing the reaction rate. Thus, there is a considerable difference between the reaction at the first branch and the same reaction at the last branch (Figure 1).



**Figure 1.** a) The reaction at the dendrimer periphery depends on whether the reaction site is close ( $v_1$ , steric effect) or far ( $v_2$ , no steric effect) from an S site that has already reacted; b) reaction at the last free site is much slower ( $v_3$ ) than in a) due to maximum steric effect.

In many instances, this difference is so large that the last branch may react at a much slower rate than that of the same reaction at the first branch, or may not even react at all. Actually, in a number of cases, the given reaction cannot proceed on all the dendrimer branches because of this variable microenvironment factor along all the “identical” reactions in a dendrimer. Therefore, a reaction must be highly efficient and proceed rapidly in quantitative yield in monomer chemistry in order to be candidate for application to dendrimer construction. If, for example, the dendrimer contains 100 terminal branches and the reaction proceeds in 99% yield, in theory, the reaction will proceed on average on 99 branches, so that no pure dendrimer of next generation will be obtained. Actually, the increase of stereoelectronic constraints as the reaction proceeds on the dendrimer branches upon divergent construction will end up with a reaction much weaker than 99% yield, and the dendrimer purity gets even worse at the following generation when the dendritic reaction sequence is repeated.<sup>19,20</sup> Even for the simplest chemical reaction, electron transfer, the potential of redox change at each branch is not exactly the same for all the dendrimer branches (they are extremely close to one another), although, for instance, with ferrocene termini, all the redox changes are observed in a single cyclic voltammetry wave.<sup>21,22</sup> The standard analytical techniques including elemental analysis, NMR, infrared and UV-vis spectroscopies, etc., are not adequate (not precise enough) to detect small defects. On the other hand, the MALDI-TOF and ESI mass spectra of dendrimers are an excellent diagnostic tool to detect dendrimer defects, but they were not always reported in the literature. Thus, divergent dendrimer syntheses in constructions involving several generations are, more or less, monodisperse, but not perfect macromolecules. This problem parallels that encountered in polymers, for which reactions are repeated at a single site, but whose length is limited by side reaction at a certain polymerization degree.<sup>23</sup>

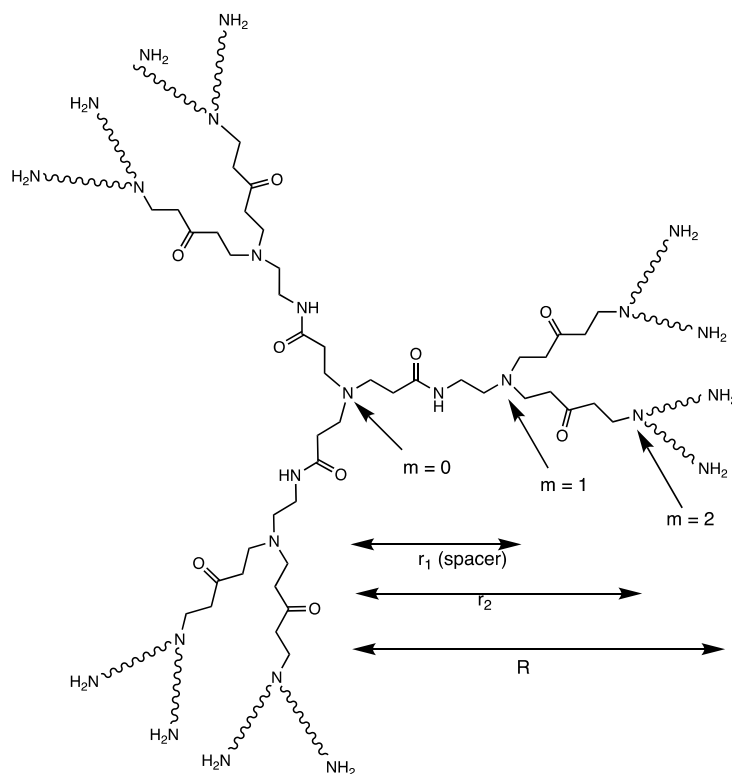
As opposed to the divergent construction, the convergent construction, more familiar to organic chemists (see, for instance, Lehn's cavities construction),<sup>24</sup> is more adequate than the divergent one to reach perfectly molecularly defined macromolecular structures, because defects produced are sufficiently different from the main product to be easily separated at each generation. As the generation increases, however, it becomes more and more sterically difficult to control reaction at the dendronic focal point, which severely limits the number of generations accessible using this method (Figure 2).<sup>19,20</sup>



**Figure 2.** Schemes of the divergent (left) and convergent (right) dendrimer constructions (equiv = equivalent) using a tridentate core and double branching. A similar scheme can be drawn with Newkome's triple branching units.<sup>25</sup>

### 3. The de Gennes Dense-packing Limit

Tomalia's poly (amidoamine) (PAMAM) dendrimers are constructed from a poly *N*-(2-aminoethyl) acrylamide core by sequences (generations) of Michael addition of an acrylate ester to an amine functionality followed by amidation of the resulting ester with ethylene diamine.<sup>10</sup> Using these PAMAM dendrimers, de Gennes reported a theoretical limit beyond which regular dendrimer construction can no longer proceed due to the bulk at the periphery.<sup>26</sup> The limit number  $m$  of generation proposed by de Gennes is given by :  $m \sim 2,88 (\ln P + 1.5)$ , in which  $P$  is the number of monomeric units. This corresponds to a maximum spatial radius  $R$  proportional to  $P$  (Figure 3).



**Figure 3.** de Gennes' model for Tomalia's poly(amido amine) (PAMAM) dendrimers. de Gennes and Hervet calculated the dense packing limit (limit generation  $m_R$ ) as a function of the spacer length  $r_1$  between two generations. Dendronic wedges beyond generation 2 are simplified by a wave between N ( $m = 2$ ) and the terminal amino groups.<sup>26</sup>

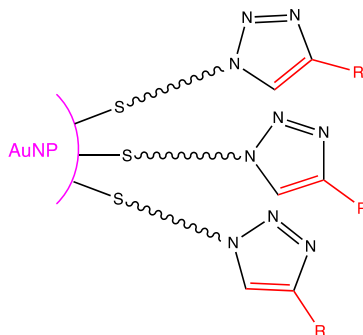
This theory ignores the possibility of branch termini backfolding. Indeed, we have reported that backfolding can release the peripheral bulk with our dendrimer construction involving hydrocarbon fragments as terminal groups (*vide infra*),<sup>27</sup> conducted using Newkome's 1  $\rightarrow$  3 type branching,<sup>25</sup> proceeding far beyond this limit. It has been suggested, however, that backfolding of dendritic termini is all the less pronounced as these terminal groups are bulkier.<sup>28</sup> With ferrocene and pentamethylferrocene dendrimer termini, our highest generations are indeed lower than with terminal double bonds,<sup>21</sup> although they still reach up to 19 000 metal-sandwich termini.<sup>29</sup>

## 4. Catalyzed and Non-catalyzed Reactions in Dendrimer Chemistry

In Sections 2 and 3, dendrimer chemistry, including the repetition of a reaction in all the dendrimer branches, has been discussed independently of any catalysis. As in other fields of molecular chemistry, reactions can be catalyzed or non-catalyzed. For instance, in the first branching reaction reported by Vögtle *et al.*,<sup>31</sup> the repetition sequence involves the non-catalyzed reaction of acrylonitrile with a di-amine producing a tetra-nitrile, followed by the difficult cobalt(II)-catalyzed reduction of this tetra-nitrile by NaBH<sub>4</sub> to a tetra-amine product, and reproduction of this sequence, but only once. This branching chemistry could not be pursued beyond the octa-nitrile, probably because of the difficulty of the catalytic step. It is only 15 years later that this dendrimer sequence was improved by replacing the Co(II) catalyst in the reduction step by Raney Ni<sup>32</sup> or Raney Co<sup>33</sup> catalyst under 8 atm H<sub>2</sub> pressure instead of NaBH<sub>4</sub>. This initial branching synthesis shows that the efficiency of some catalytic reactions depends on the dendrimer generation, a trend that has been verified in various instances in our laboratories.<sup>34</sup> Another notable aspect is that late-transition metal nanoparticles (NPs) (here of Raney type) can accommodate high-generation dendritic chemistry,<sup>32,33</sup> because NPs easily penetrate inside dendritic frameworks, which is not the case of larger molecular catalysts. This gave rise to a rich dendrimer-encapsulated catalytic NP chemistry,<sup>18,35-38</sup> whereby even dendrimer-encapsulated single atoms and sub-nanoclusters can be found.<sup>39-41</sup> Finally, “click chemistry”,<sup>42</sup> involving Cu-catalyzed alkyne-azide Coupling (CuAAC),<sup>43-47</sup> hydrocarbon metathesis<sup>44-47</sup> and late-transition-metal-catalyzed cross-coupling reactions<sup>45-47</sup> most of the time, have altogether considerably improved the proportion of catalyzed reactions in organic chemistry, particularly since the 2000s,<sup>46,47</sup> including dendrimer design and synthesis.<sup>11,12,20,27,48-51</sup>

## 5. Gold Nanoparticles: One-pot Multiple C-C and C-N Bond Formations

Gold nanoparticles (AuNPs) have been the subject of an immense and multifold research area with applications in biomedicine, optics, electronics, sensing, catalysis and materials science, most often due to their plasmonic properties.<sup>52,53</sup> AuNPs are best synthesized and stabilized *inter alia* using alkylthiolate ligands with low polydispersity sizes in the 2-10 nm range,<sup>54</sup> in which the visible-light-induced plasmon is active. Then, partial ligand exchange is conducted following an associative mechanism at the AuNP surface in order to introduce a small proportion of functional thiolate that is all the lower as the ligand chain is longer, due to bulk.<sup>55</sup> Under well-defined conditions, atomically precise AuNPs, called Au nanoclusters (AuNCs), have been synthesized as well, isolated after chromatographic purification and identified.<sup>56</sup> From the functional terminal groups of some AuNP ligands, a variety of further functionalization have been carried out such as nucleophilic substitution, nucleophilic addition, addition to carbonyls, substitution at the carbonyls, acid-base reactions, radical polymerization, and olefin metathesis, and they have been thoroughly reviewed.<sup>57</sup> In these reactions of AuNPs, the problems discussed in the above sections in dendrimer chemistry remain the same, although the number of reactive branches is sometimes lower than in dendrimers. Noteworthy is the recently increased proportion of catalyzed reactions involving late-transition-metal-catalyzed cross C-C couplings<sup>58</sup> and click reactions<sup>59</sup> in AuNP chemistry (Figure 4).

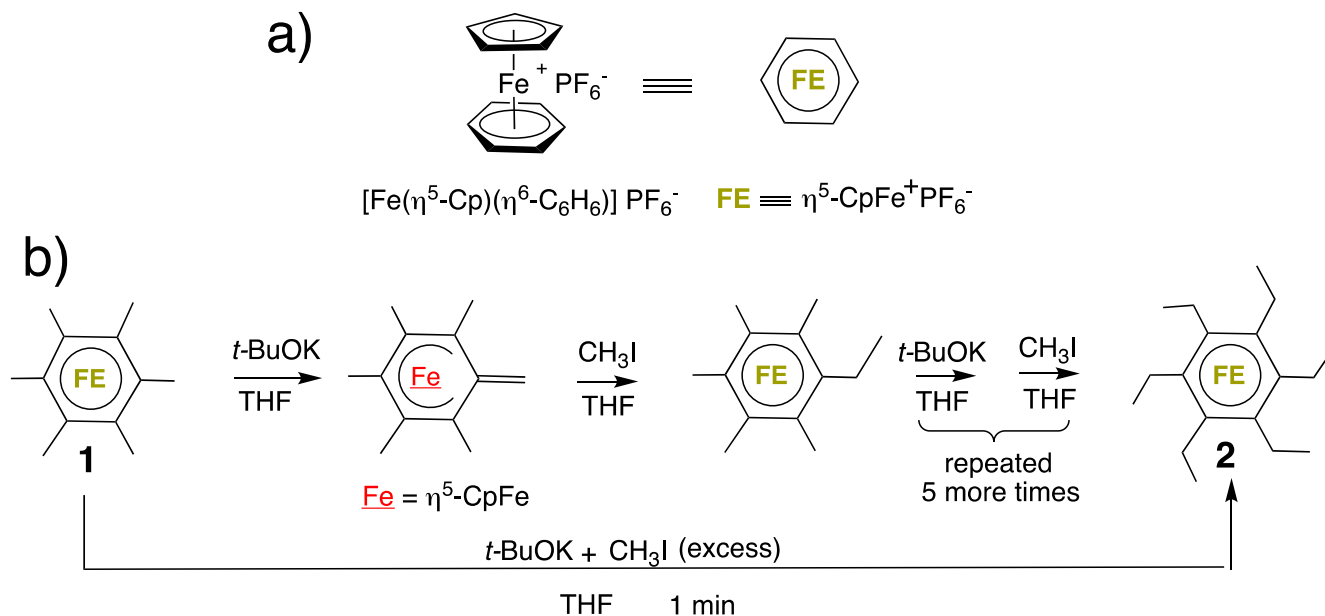


**Figure 4.** The Cu-catalyzed azide-alkyne cycloaddition (CuAAC) “click” reaction is an efficient way to functionalize AuNPs upon successive one-pot C-N bond formation on the different tethers.

## 6. Fe-induced One-pot Multiple C-C Bond Formation Toward Molecular Stars and Dendrimers

In the chemistry of the sandwich complexes  $\text{CpFe}(\eta^6\text{-arene})$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ), arene activation towards nucleophiles might be comparable to that known in the  $[\text{Cr}(\eta^6\text{-arene})(\text{CO})_3]$  series,<sup>60,61</sup> but, in fact, it strongly depends on the metal oxidation state.<sup>62</sup> Whereas the neutral 19-electron complexes  $\text{CpFe}(\eta^6\text{-arene})$ <sup>63,64</sup> are subjected to transition-metal radical chemistry,<sup>65</sup> the isostructural 18-electron complexes undergo more facile nucleophilic addition on the arene ligand than in the  $[\text{Cr}(\eta^6\text{-arene})(\text{CO})_3]$  family, due to the positive charge in the complexes  $[\text{CpFe}(\eta^6\text{-arene})]^+\text{PF}_6^-$  that is partly delocalized onto the ligands, and consequently the benzylic hydrogen atoms are acidic.<sup>61,66</sup>

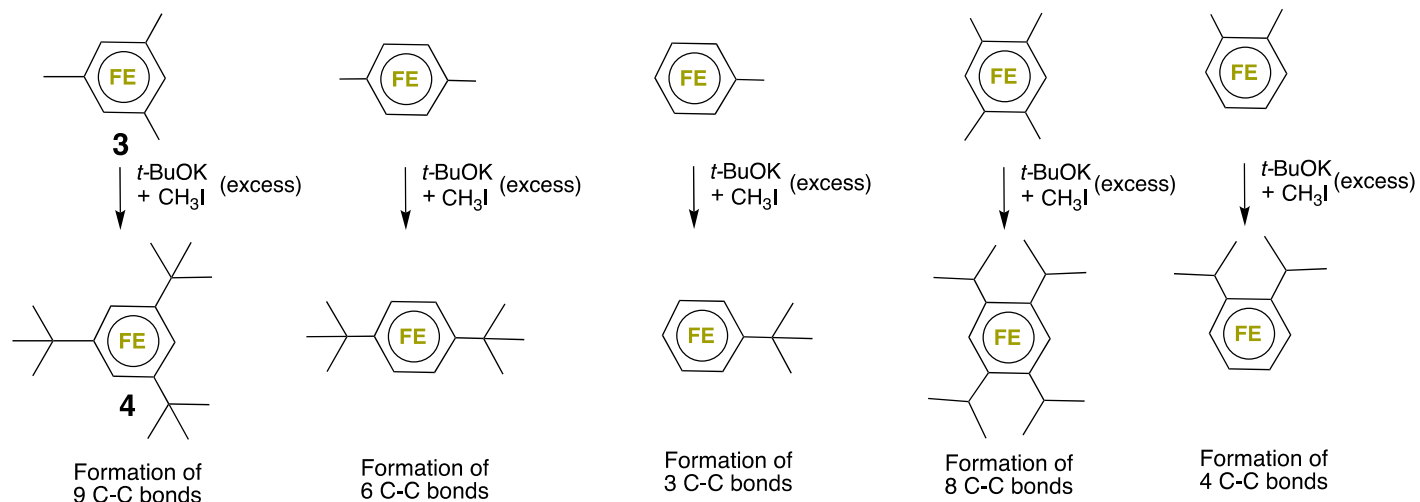
Deprotonation of the  $[\text{CpFe}(\eta^6\text{-arene})]^+\text{PF}_6^-$  salts by *t*-BuOK, in which the arene ligand bears a variable number of methyl groups, was shown to give the methylene cyclohexadienyl complex resulting from deprotonation at a benzylic methyl group, as determined *inter alia* by the X-ray crystal structure, with arene =  $\text{C}_6\text{Me}_6$ , of the ferrocene-like thermally stable complex  $[\text{CpFe}(\eta^5\text{-C}_6\text{Me}_5\text{CH}_2)]$ . Mild nucleophilic properties of the exocyclic methylene, in the latter, toward a variety of carbon, silicon, phosphorous and metal-complex electrophiles, allow many functionalization reactions. This sequence of deprotonation followed by nucleophilic reaction was extended to possible *in situ* repetition of the reaction when the complex  $[\text{CpFe}(\eta^6\text{-C}_6\text{Me}_6)]^+\text{PF}_6^-$  **1** was mixed in THF with a two-fold molar excess of *t*-BuOK and MeI. A high (virtually quantitative) yield of  $[\text{CpFe}(\eta^6\text{-C}_6\text{Et}_6)]^+\text{PF}_6^-$  **2**, was obtained, resulting from six spontaneous *in situ* deprotonation-alkylation sequences (Figure 5).



**Figure 5.** a) Side tri-dimensional (left) and top/planar (right) views representing the yellow sandwich complex  $[\text{CpFe}(\eta^6\text{-C}_6\text{H}_6)]^+\text{PF}_6^-$ ; Fe(II) herein has 18 valence electrons, and the complex is  $d^6$ , isolobal with ferrocene;<sup>67</sup> b) compared stepwise deprotonation-methylation reactions (top) and one-pot spontaneous formation of six carbon-carbon bonds using a two-fold molar excess of a mixture of  $t\text{-BuOK}$  and  $\text{CH}_3\text{I}$  in THF (bottom).

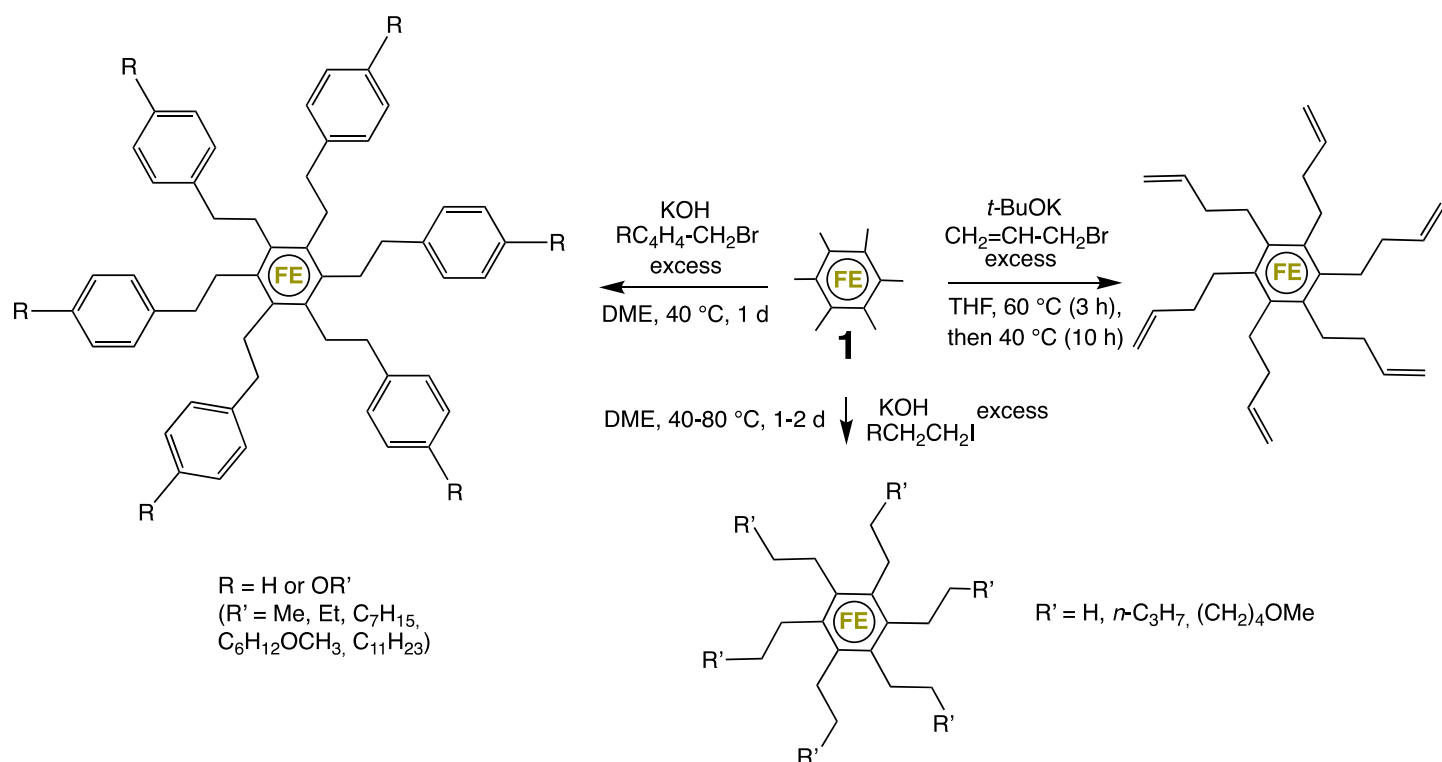
This selectivity shows the superiority of the organometallic reaction over the organic reaction between  $\text{CH}_3\text{I}$  and  $t\text{-BuOK}$ , due to the excellent basic properties of  $t\text{-BuOK}$  compared to its well-known poor nucleophilic properties.<sup>68</sup> However, a two-fold molar excess of base and electrophile was utilized (also throughout the paper and equations) in order to take into account this minor organic reaction. The deprotonation-methylation sequence that is spontaneously occurring six times in the one-pot reaction<sup>6</sup> can also be reproduced stepwise by conducting the twelve individual reactions (Figure 5).<sup>63</sup> Whereas the reaction is limited to only one deprotonation-methylation sequence at each benzylic carbon atom, due to the steric bulk caused by the two neighboring methyl groups of the  $\text{C}_6\text{Me}_6$  ligand, the same one-pot reaction conducted with the mesitylene complex  $[\text{CpFe}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)]^+\text{PF}_6^-$ , **3**, is not marred by this steric limitation at each benzylic methyl group, and spontaneously leads to nine deprotonation-methylation reactions, corresponding to the presence of the nine benzylic hydrogen atoms. This reaction ends with the 1,3,5-tris-*ter*-butyl benzene complex  $[\text{CpFe}(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{(C-}t\text{-Bu)}_3)]^+\text{PF}_6^-$ , **4**. With the *o*-xylene and durene complexes, the steric constraint is intermediate with only one methyl group neighbor, and two deprotonation-methylations are spontaneously obtained, giving the 1,2-di-isopropyl- and 1,2,4,5-*tetra*-isopropylbenzene complexes respectively (Figure 6).<sup>66</sup>



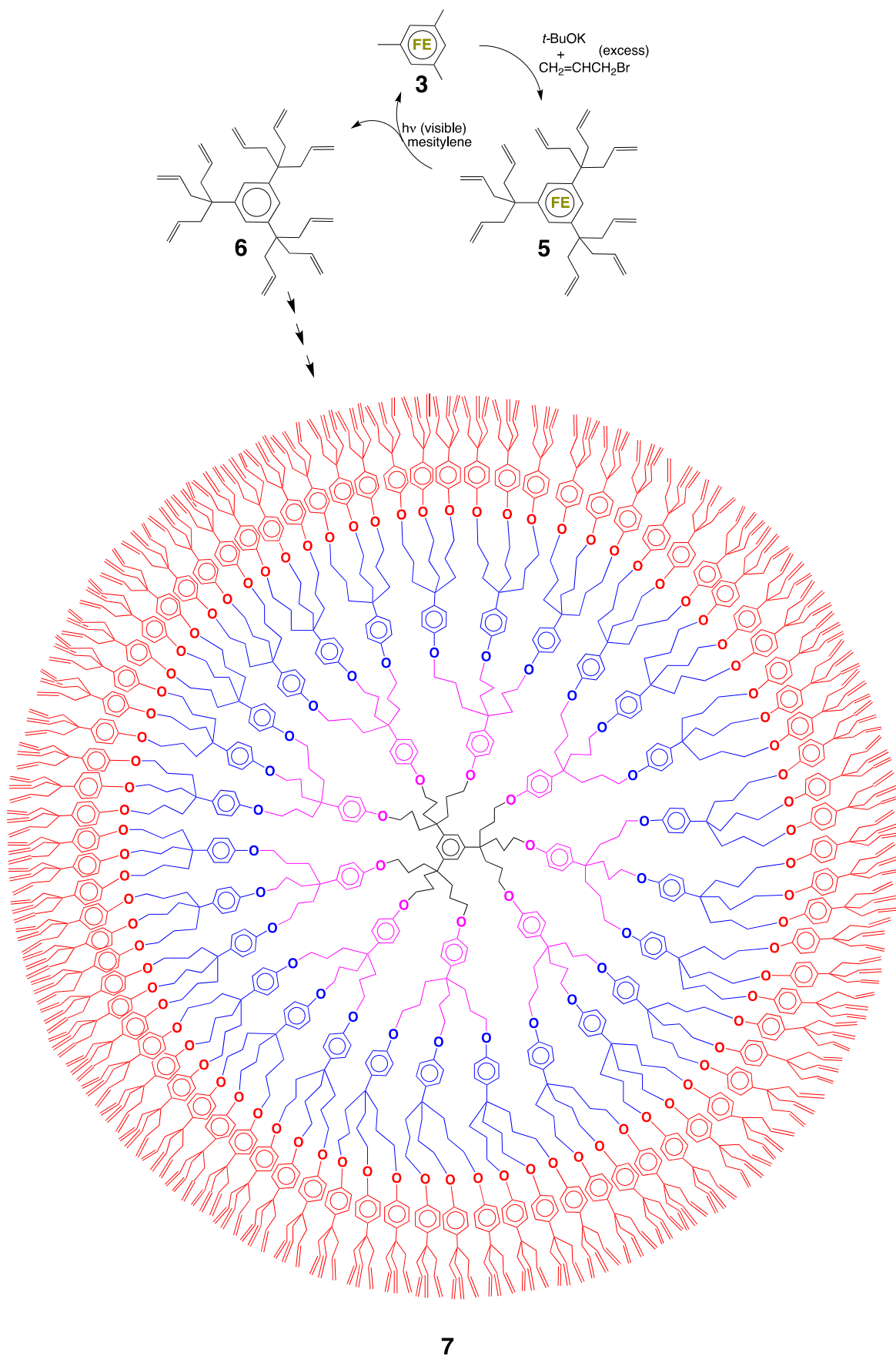


**Figure 6.** One-pot CpFe<sup>+</sup>-induced formation of multiple C-C bonds. These reactions of the yellow PF<sub>6</sub><sup>-</sup> salts are fast under ambient conditions.

This system was extended to allyl<sup>69-71</sup> and benzyl<sup>66,72</sup> bromides that do not contain β-hydrogen atom vs. the halogen in the halogeno-derivatives. Due to dehydrohalogenation by *t*-BuOK, these reactions do not work with alkyl iodides containing β-H atoms, although this problem was circumvented using KOH instead of *t*-BuOK, and star-shaped complexes [CpFe(η<sup>6</sup>-C<sub>6</sub>R<sub>6</sub>)]<sup>+</sup>PF<sub>6</sub><sup>-</sup> with long R chains were also obtained in a single pot upon mixing the complex with an excess of base and electrophile<sup>73</sup> (Figure 7).



**Figure 7.** One-pot formation of 6 C-C bonds leading to functional star-shaped molecules by reaction of **1** with an excess of *t*-BuOK (in THF) or KOH (in DME) and various carbon electrophiles.



**Figure 8.** One-pot synthesis of **5** from **3** by formation of nine C-C bonds and its utilization in dendrimer synthesis.

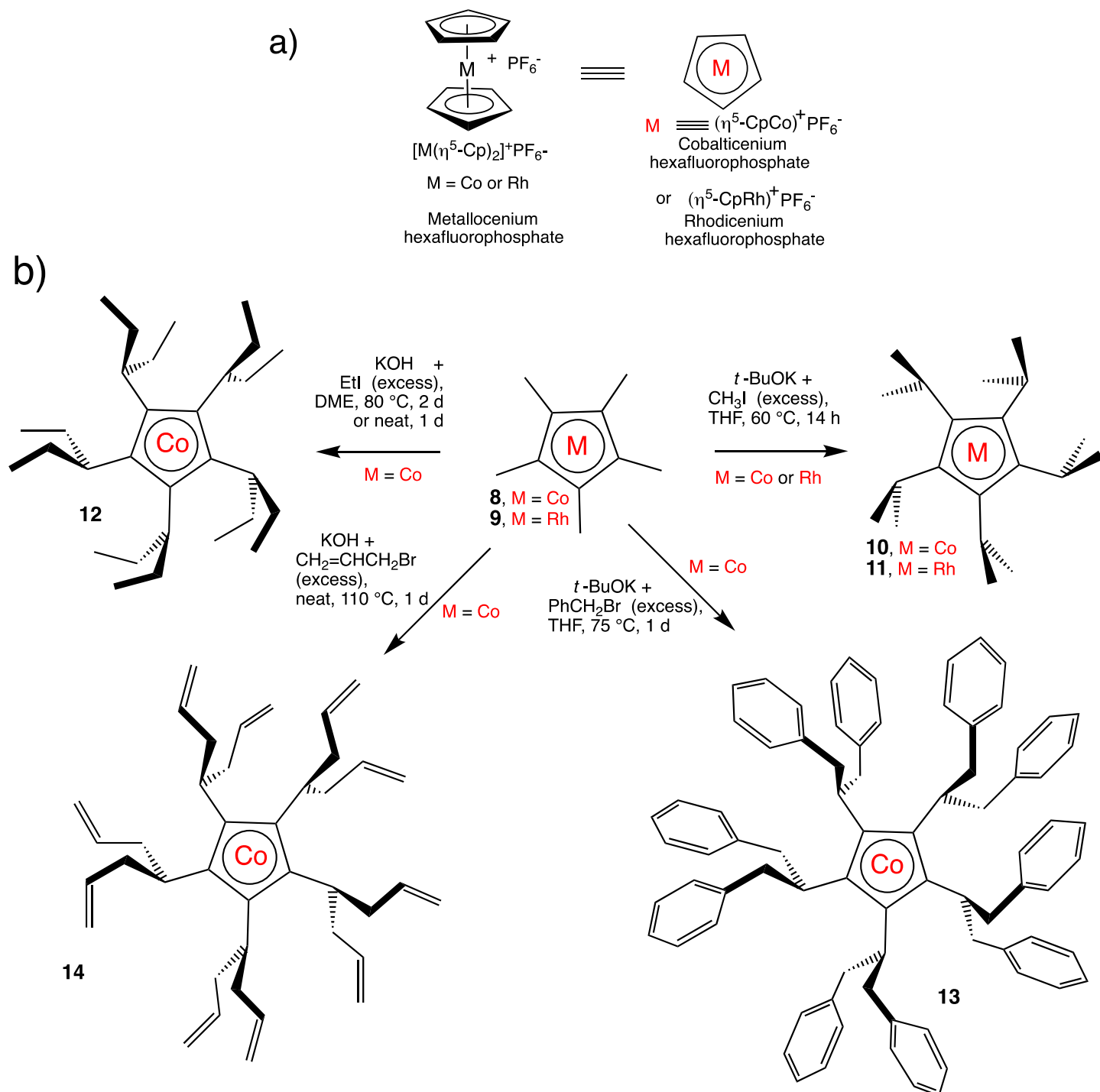
The most useful reaction among all these one-pot multiple C-C bond-formation reactions is that of the mesitylene complex **3** with allyl bromide involving the use of either *t*-BuOK or KOH, leading to the non-allylated complex  $[\text{CpFe}(\eta^{6-1,3,5-\text{C}_6\text{H}_3\{\text{C}(\text{CH}_2\text{CH}=\text{CH}_2)_3\}_3)^+\text{PF}_6^-]$ , **5**. The latter can be easily de-coordinated using visible light and mesitylene,<sup>71</sup> regenerating **3** and yielding the metal-free nona-allyl dendritic core  $1,3,5\text{-C}_6\text{H}_3\{\text{C}(\text{CH}_2\text{CH}=\text{CH}_2)_3\}_3$ , **6**. Thus, this one-pot nona-allylation of **3** leading to **6** is cyclic, using a catalytic-like quantity of the  $\text{CpFe}^+$  group, initially provided by complexation of mesitylene using ferrocene.<sup>61,74</sup> Note that the 3-fold branching at the three benzylic positions in mesitylene is the start of the  $1 \rightarrow 3$  branching strategy initiated by Newkome *et al.* in his seminal “arborol” synthesis.<sup>75</sup> This strategy is continued upon branching at the focal point a *p*-phenoltriallyl dendron,  $\text{HOC}_6\text{H}_4\text{C}(\text{CH}_2\text{CH}=\text{CH}_2)_3$ , synthesized by a one-pot reaction of the ethoxytoluene complex  $[\text{CpFe}(\eta^{6-p}\text{-EtO-C}_6\text{H}_4\text{CH}_3)^+\text{PF}_6^-]$ , with excess allyl bromide and *t*-BuOK. One of the third-generation dendrimers synthesized in this way, **7**, is shown in Figure 7.<sup>76</sup> Such dendrimers present the molecular peak in MALDI TOF mass spectrometry for the second-generation 81-allyl dendrimer, although a small peak corresponding to one missing tripod is also observed. On the other hand, for the third-generation 243-allyl dendrimer, the molecular peak itself is missing (although defects are not observable by <sup>1</sup>H NMR, given their very low proportion),<sup>27</sup> illustrating the differences in identical reactions at the dendrimer periphery pointed out here in the first section. The applications of these dendrimer series, however, were obtained from the zeroth and first-generation 27-allyl and 81-allyl dendrimers, respectively (in particular sensing and catalysis<sup>34</sup>) (Figure 8).

## 7. Co- vs. Rh-induced One-pot Formation of up to 20 C-C Bonds

The above strategy involving one-pot Fe-induced multiple C-C bond formation can be switched from a C6 aromatic ligand to a C5 cyclopentadienyl (Cp) ligand ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) if the robust 18-electron structure of the transition-metal center, indispensable for such an energetic process, is preserved. Since the C6 aromatic ligands brings 6  $\pi$  electrons to the metal, a C5-cyclopentadienyl bringing only 5  $\pi$  electrons to the metal will require, in order to reach the 18-electron count, a CpM fragment in which the metal will bring one more valence electron than CpFe, that is a CpCo or RhCp fragment (Figure 8) in which the metal reaches the 13-electron count.<sup>47</sup>

Indeed, the  $\text{PF}_6^-$  salts of the cations cobalticinium  $[\text{CoCp}_2]^+$ <sup>77</sup> and rhodicinium  $[\text{RhCp}_2]^+$ <sup>78</sup> and their pentamethylcyclopentadienyl analogues  $[\text{MCp}^*_2]^+$ <sup>79</sup> and  $[\text{MCp}^*\text{Cp}]^+$ ,  $\text{M} = \text{Co}^{\text{80}}$  or  $\text{Rh}$ ,  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ,<sup>81</sup> isolobal<sup>82</sup> to  $[\text{CpFe}(\eta^6\text{-arene})]^+\text{PF}_6^-$ , are very robust complexes. Cationic sandwich 18-electron Co and Rh complexes of these series are all the more robust as their cyclopentadienyl ligands are permethylated ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ). The methyl substituents of the  $\text{Cp}^*$  ligand are acidic, given the overall positive charge of these complexes that can be deprotonated to give neutral tetramethyl fulvene complexes  $[\text{M}(\eta^4\text{-C}_4\text{Me}_4=\text{CH}_2)\text{Cp}^\&]$ ,  $\text{M} = \text{Co}$  or  $\text{Rh}$ ,  $\text{Cp}^\& = \text{Cp}$  or  $\text{Cp}^*$ .<sup>83</sup>

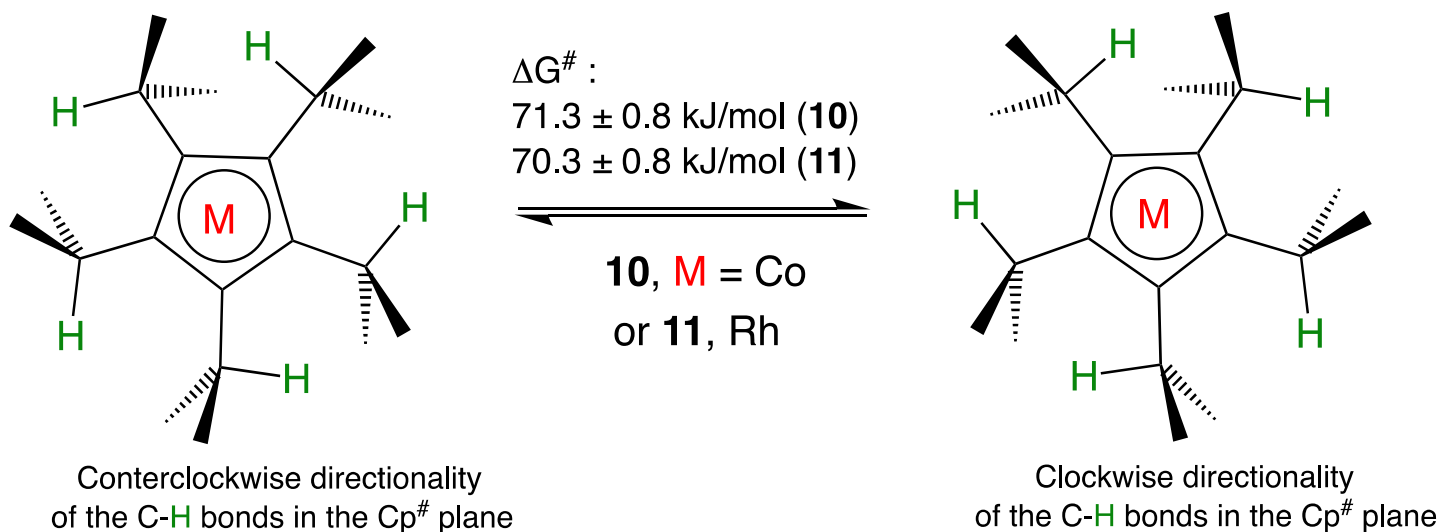
The exocyclic methylene groups of these fulvene complexes have nucleophilic properties and, thus, react with electrophiles. In this way, one remains in the same situation as with the above complexes,  $[\text{CpFe}(\eta^6\text{-arene})]^+\text{PF}_6^-$ , except that the acidity of these complexes is somewhat weaker than that of the complexes  $[\text{CpFe}(\eta^6\text{-arene})]^+\text{PF}_6^-$ , because, in a series of cationic isolobal complexes, the even ligands are more acidic than the odd ones.<sup>84,85</sup> Nevertheless, the complexes  $[\text{MCp}^*\text{Cp}]^+\text{PF}_6^-$ ,  $\text{M} = \text{Co}$  (**8**) and  $\text{Rh}$  (**9**) both react in one-pot with excess *t*-BuOK and  $\text{CH}_3\text{I}$  in THF at 60 °C for 14 h to yield the complexes  $[\text{MCp}^\#\text{Cp}]\text{PF}_6^-$ ,  $\text{Cp}^\# = \eta^5\text{-C}_5(\text{iPr})_5$ ,  $\text{M} = \text{Co}$  (**10**) and  $\text{Rh}$  (**11**) (Figure 9).<sup>81,83</sup>



**Figure 9.** a) Side (left) and top (right) molecular views representing the sandwich metallocenium hexafluorophosphate salts; b) deca-alkylation and deca-functionalization of the 1,2,3,4,5-pentamethylmetallocenium salts **8** and **9**; M =  $\eta^5\text{-CpCo}^+\text{PF}_6^-$  (**8**) or  $\eta^5\text{-CpRh}^+\text{PF}_6^-$  (**9**), by one-pot formation of 10 C-C bonds.

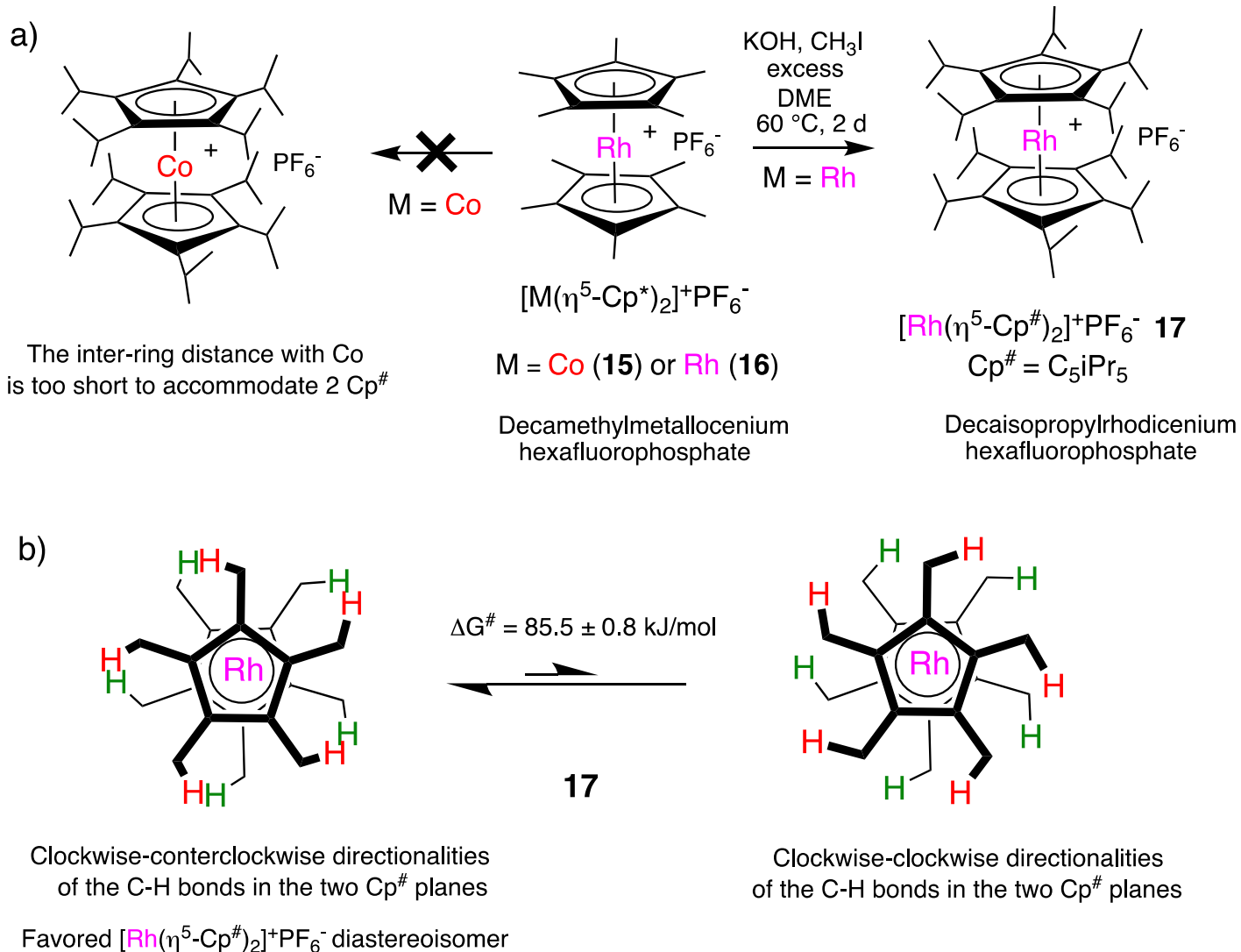
These reaction conditions using **8** and **9** are more drastic than with the complexes  $[\text{CpFe}(\eta^6\text{-arene})]^+\text{PF}_6^-$ . However, these reactions are completed with double branching at each exocyclic carbon, whereas such double branching at the benzylic carbons was not possible in a one-pot reaction with **1** in which each methyl group is also surrounded by two neighboring methyl groups. Clearly, the angle between exocyclic

C-C bond, 60° in **1**, but raising to 72° in **8** and **9**, plays a crucial role in controlling the available bulk during the multiple C-C bond formation. This one-pot formation of a 10 C-C bond leading to **10** and **11** was extended with **8** to EtI using KOH in DME instead of *t*-BuOK in order to avoid dehydroiodation, yielding **12**, and to PhCH<sub>2</sub>Br and CH<sub>2</sub>=CH-CH<sub>2</sub>Br yielding **13** and **14** respectively, providing a family of deca-functionalized cobalticenium salts.<sup>81,83</sup> These complexes exhibit a paddle-wheel shape with single directionality of the five remaining exocyclic C-H bonds with restricted rotation barriers, measured by <sup>1</sup>H NMR in *o*-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub> (71.3±0.8 kJ/mol for **8**; 70.3±0.8 kJ/mol for **9**, Figure 10).



**Figure 10.** Restricted rotation of the *i*-Pr groups measured by <sup>1</sup>H NMR. The X-ray crystal structure of **10** shows the staggered conformation of the two fully parallel cyclopentadienyl rings. The similarity of the rotation barriers (Co vs. Rh) signifies that the inter-ring distance change between Co and Rh is not involved in this barrier.

Attempts to extend the reaction with CH<sub>3</sub>I and *t*-BuOK to the 18-electron decamethyl metallocenium complexes depend on the nature of the metal. With the Co sandwich complex **15**, the one-pot reaction cannot proceed to completion of the double branching, and a mixture of complexes was obtained corresponding to an average of nine C-C bond formation (a maximum of 14 C-C bonds were formed upon successive reactions). The too-small distance between the two Cp<sup>#</sup> planes is responsible for the lack of possible accommodation of two penta-*i*-Pr cyclopentadienyl ligands, Cp<sup>#</sup>. On the other hand, in the Rh sandwich complex **16**, the larger size of the rhodium atom compared to Co results in a larger inter-Cp<sup>#</sup> plane, and the one-pot reaction of **16** with excess of both CH<sub>3</sub>I and *t*-BuOK does cleanly proceed to the formation of 20 C-C bonds, yielding the deca-*i*-Pr rhodocenium salt [RhCp<sup>#</sup><sub>2</sub>] PF<sub>6</sub><sup>-</sup>, **17** (Figure 11).<sup>83,86</sup>



**Figure 11.** a) One-pot formation of 20 C-C bonds upon synthesis of deca-*i*-Pr rhodocenium hexafluorophosphate **17** from decamethyl rhodocenium hexafluorophosphate **16**, whereas the too-short inter-ring distance does not permit such a reaction with the Co analogue **15** ; b) preferred diastereoisomer of the deca-*i*-Pr rhodocenium salt **17** (left) interconverting with *i*Pr group rotation of the Cp<sup>#</sup> ligands only above 130 °C at 200 MHz. The 20 methyl groups of the 10 *i*Pr substituents of the Cp<sup>#</sup> rings in **17** are omitted for clarity.

## 8. Concluding Remarks

In dendrimers and gold nanoparticles, the functionalization of the different equivalent terminal branches occurring by C-C or C-element bond formation proceeds with the same reaction, AAAA...(compare to polymerization, AAAA...), but the reaction rate slows down in relatively large dendrimers as bulk increases at the dendrimer periphery, although, with flexible termini, backfolding partly avoids periphery crowding. Polymethylated late-transition-metal sandwich complexes are known as electron reservoir systems<sup>87,88</sup> and serve as redox references.<sup>89</sup> Their cationic forms also behave as proton reservoir systems,<sup>90</sup> allowing one to perform one-pot “spontaneous” multiple deprotonation-alkylation sequences with ABABABAB...reactions up to the formation of 20 C-C bonds. It is this original one-pot multiple C-C bond formation principle, occurring

spontaneously in the presence of an excess of base and electrophile, that efficiently yielded molecular stars and dendritic cores, with further functionalization to dendrons and dendrimers. It was noted in the introduction that some early dendrimer families were constructed by C-N bond formation. The principles governing reaction rates of bond formations in dendrimers and gold nanoparticles discussed in Section 2 are indeed fairly general, and many other types of dendrimers including large dendrimers were constructed, most often according to the divergent method, using bond formation between a variety of elements (B, C, Si, Ge, N, P, O, etc.), as illustrated and summarized in the Majoral-Caminade early review.<sup>91</sup>

## 9. Competing Interests

There are no competing interests to declare.

## 10. Acknowledgements

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## Author's Biography



**Didier Astruc**, born in Versailles, studied in Rennes where he passed two theses with Prof. René Dabard before post-doctoral studies with Prof. Richard R. Schrock at MIT, Cambridge, Mass. Then, after several years as a CNRS Master of Research in the University of Rennes, he moved to the University of Bordeaux, where he has been Professor of Chemistry since 1983 and a Member of the Institut Universitaire de France since 1995. In 1990-1991, he spent a sabbatical year with Prof. K. Peter C. Vollardt at the University of California, Berkeley. He is the author of 600 publications and of *Electron Transfer and Radical Processes in Transition Metal Chemistry* (VCH, New-York, 1995, prefaced by Henry Taube) and *Organometallic Chemistry and Catalysis* (Springer, Heidelberg, 2007 ; French versions in 2001 and 2013, EDP Sciences, Les Ullis). His present interests, with his research group, are at the interplay between macromolecules and small nanoparticles and their applications, most recently, in drug delivery and energy conversion.

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