Organoiron-mediated synthesis and redox activity of organoiron-containing dendrimers

Didier Astruc *, Yanlan Wang, Amalia Rapakousiou, Abdou Diallo, Rodrigue Djeda, Jaime Ruiz, Catia Ornelas

ISM, Univ. Bordeaux, UMR CNRS 5255, 351 Cours de la Libération, 33405 Talence Cedex, France

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Dedicated to Dr. Claude Lapinte, in recognition of his excellent contribution to organometallic chemistry and materials science.

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1. Introduction

Organoiron synthesis and redox activity of organoiron complexes are crucial to the development of organoiron materials with unusual properties, as demonstrated by Claude Lapinte and colleagues at the University of Rennes [1,2]. In this micro-review, we emphasize two key aspects of organoiron dendrimers that were essentially developed in our research group: (i) organoiron-mediated synthesis and (ii) redox properties and applications of organoiron dendrimers. These two fields are related, because organoiron activation depends on the metal oxidation state and in turn the redox properties of organoiron dendrimers induce new functions and applications of these nanomaterials. Since their seminal discovery by the groups of Newkome [3], Tomalia [4] and Denkewalter [5], dendrimers are a growing field of supramolecular nanochemistry [5–10] with multiple applications involving mostly sensors [11,12], energy-related nanomaterials [13–15], nanomedicine [16–20], and catalysis [20–22]. Their construction must be carefully designed using selective reactions, in particular involving the branching strategy [23], and their redox properties have specific connections with their biological, catalytic, and nanomaterials applications [24].

2. Redox and activation properties of organoiron sandwich complexes

Besides the classic ferricenium/ferrocene redox system involving the relatively fragile and reactive 17-electron ferricenium cation, cationic organoiron sandwich complexes with the 18-electron electronic configuration are robust, which allows easy handling towards organic and organoiron syntheses [25]. Their most classic structures are the mixed ligand series [FeCp(η6-arene)]2+/+0 with a large variety of arene ligands [26,27] including polymers [28] and dendrimers [29] and the symmetrical [Fe(η6-arene)]2 family [30] that is restricted to benzene and polymethylated arene derivatives. Both families are known with the three oxidation states, the [FeCp(η6-arene)]2+/+0 with the oxidation states Fe(III), Fe(II) and Fe(I) [27,31], and the series [Fe(η6-arene)]2+0 [32] with the oxidation states Fe(II), Fe(I) and Fe(0), although the two latter oxidation states are known only with the C6Me6 ligand. Although the [Fe(η6-arene)]2+ family has yielded applications to aromatic and cyclohexadiene syntheses involving the different oxidation states indicated above [30,32],
by far the most versatile and useful system has been the \([\text{FeCp}^\eta(\eta^6-\text{arene})]^\text{II}\) series. The electron-rich neutral series provides "electron-reservoir" systems [33] that activate substrates by ligand substitution [34] or electron transfer [33], whereas the cationic 18-electron complexes are powerful activators of deprotonation [35] (a principle that has been extended to the activation by CpCo [36]) and nucleophilic substitution [37] at the various arene ligands (Fig. 1).

3. Organoiron mediated syntheses of dendritic cores and dendrons

Both organoiron activation of arenes in the isostructural cat-ionic 18-electron and neutral 19-electron configurations lead to benzylic C–H activation of the arene ligands in the mixed-sandwich complexes that allows further functionalization of these arene ligands leading to carbon–carbon or carbon-element bond formation. Such a reaction in the cationic 18-electron series requires the action of a base such as KOH or t-BuOK under ambient conditions, whereas the reaction of the 19-electron analogues requires simple contact with dioxygen or air at or below room temperature (Scheme 1).

For single C–H activation (Scheme 1), the 19-electron complexes provide somewhat cleaner reactions, whereas for multiple C–H activation of benzylic hydrogens, the cationic route is preferred, because it can be conducted in situ. This cationic route is in fact so remarkable that, in the presence of an electrophile such as allyl bromide, it leads to 9 consecutive C–H activation reactions in situ under ambient conditions with the mesitylene complex, each deprotonation being followed by a nucleophilic substitution of the halide in the organic halide. This iterative arene activation reaction was first disclosed in 1979 with the complex \([\text{FeCp}(\eta^6-\text{C}_6\text{Me}_5)]^\text{II}\) and methyl iodide in the presence of t-BuOK and occurred spontaneously in about one minute to yield the hexaethylbenzene complex [38]. Later this reaction was also extended to allyl bromide and led to the extremely bulky dodecaallylbenzene complex upon 12 deprotonation-allylation sequences in situ [39]. Further dendrimer construction was achieved by the cationic charge [40]. This situation paralleled on the cationic \([\text{FeCp}(\eta^6-\text{C}_6\text{Me}_5)]^\text{II}\) and methyl iodide in the presence of t-BuOK, which was easier because of the reduced congestion [36]. In 1979, however, dendrimer chemistry was not yet born, although these iteration reactions were precursors as well as Vögtle's iteration [39].

The \(\text{CFe}^\text{II}\) induced nona-allylation of mesitylene in 1D was chosen, however, to develop dendrimer syntheses because of its easy completeness under ambient conditions, and the facile visible-light-induced arene exchange of the nonaallylated \(\eta^5\)-arene ligand by mesitylene in 6 recycling the starting material in this way (Scheme 2).

![Fig. 1. Iron sandwich complexes that are useful for both redox processes and arene ligand activation (the counter anion of the salts usually is PF\(_6\)): 1A is known with various R\(_x\) groups (n = 1: large variety of R; n = 1–6: R = Me) and undergoes nucleophilic reactions and deprotonation in benzylic position; 1B is stable with n = 0–2; in particular the redox system 1B to 2B is a redox system known as electron reservoir; the neutral 19-electron form reacts with O\(_2\) yielding H-atom abstraction; 2A undergoes hydride addition follow by another nucleophile addition to form functional cyclohexadiene complexes; 2B is stable for n = 0–2 and for n = 0 the 20-electron complex reacts with O\(_2\) with double H-atom abstraction to form an 18-electron \(\text{Fe}(0)\)-o-xylene complex [25].](image-url)

Extension of this chemistry to the arene ligand in \([\text{FeCp}(\eta^6-p\text{-ClC}_6\text{H}_4\text{CH}_3})^\text{III}\] \([\text{PF}_6]\), 8, easily available from \([\text{FeCp}(\eta^6-p\text{-ClC}_6\text{H}_4\text{CH}_3})^\text{III}\] \([\text{PF}_6]\) by reaction with ethanol in the presence of t-BuOK, provided in good yield the very useful dendron p-HO-(C\(_x\)-CH=CH\(_2\))\(_n\), 9, resulting from 8 steps in a single pot reaction [37a].

4. Dendrimer constructions

Further dendrimer construction was achieved upon hydrosilylation of the 9 double bonds of 7 by HSi(CH\(_2\))\(_n\)Cl followed by 1 → 3 connectivity by a Williamson reaction in the presence of the dendron, iodide and potassium carbonate (Scheme 3). This sequence was iterated 9 times, which allowed reaching the 9th dendrimer generation; this set of reaction sequences achieved the largest known dendrimers, although dendritic construction proceeded essentially inside the dendrimers due to peripheral steric bulk and backfolding of the termini after the 6th generation involving much longer reaction times and an increased number of defects [37b]. Other remarkable variations involved cross metathesis of the terminal dendrimer double bonds with acrylic acid and acrylates selectively yielding trans-olefins [40], or CuAAC "click" reaction achieved between the polyazido dendrimer with a propargylated dendron [41]. Both of these divergent dendrimer syntheses, the metathesis and "click" methods, were efficiently iterated yielding large dendrimers.

5. Organoiron dendrimers and their redox activity

Dendrimers terminated by ferrocenyl groups are the prototype of organoiron-containing dendrimers [42–45]. They were shown to serve as biosensors for instance for NADPH using the Fe(II)/Fe(III) redox interconversion with good electrocatalytic performances [45]. With amidoferrocenyl termini, dendrimers were shown early on to be excellent sensors for the redox recognition of oxo-anions such as H\(_2\)PO\(_4\) and HSO\(_4\) with positive dendritically effects, i.e. better recognition as the dendrimer generation increases. As such, they proved to be excellent exoreceptors [45]. Again, this redox recognition was based on the Fe(II)/Fe(III) interchange, electrostatic interaction between the ferrocenium cation and the recognized oxo-anion being one of the key sensing factors in synergy with the dendrimer topological effect [46]. With dendrimers terminated by the cationic redox groups \([\text{Fe}(\eta^5-C_6\text{Me}_5)(\eta^6-C_6\text{H}_4\text{NHR})]^\text{III}\] \([\text{PF}_6]\) and linked to the core by amino groups, the oxidation states that are involved in redox sensing are Fe(II) and Fe(I), because the latter is much more readily accessible upon cathodic reduction than the far Fe(III) state due to the cationic charge [47]. This situation paralleled on the cationic iron complexes to the 19-electron species [44b]. Giant ferrocenyl-terminated dendrimers were constructed with up to 15000 ferrocenyl termini upon lengthening the terminal tethers in order to minimize bulk at the periphery (Fig. 2) as models of molecular batteries.

Such large ferrocenyl dendrimers were shown to "breath" between their Fe(II) and larger Fe(III) forms due to repulsion among charged redox-active termini, and this process was demonstrated using Atom Force Microscopy (AFM) and Electron Force Microscopy (EFM) [48]. Another interest of the redox activity of ferrocenyl-terminated dendrimers is their ability to reduce HAuCl\(_4\) to dendrimer-stabilized Au nanoparticles, a property that they share with other dendrimers [49].
6. Mixed-valent dendrimers and the stabilization of gold nanoparticles

The oxidation of giant ferrocenyl dendrimers to their ferricenium analogue allowed to synthesize mixed-valent dendrimers upon mixing the ferrocenyl and ferricenium dendrimers, and therein the distribution of Fe(II) and Fe(III) termini was given by the statistics of a binomial law (Fig. 4) \[48\].

With diferrocenylsilyl-terminated such as \[12\] (or its diamagnetic precursor), cyclic voltammetry shows two well-separated ferrocenyl waves related to the electronically and electrostatically interacting ferrocenyl centers \[50\].

With small dendritic frameworks containing alternating ferrocenyl and pentamethylferrocenyl dendrimers, precise mixed-valent \[51\] Fe(II)–Fe(III) dendrimers such as \[13\] were isolated as well as the all-Fe(II) and all-Fe(III) dendritic complexes, although the ferrocenyl and pentamethylferrocenyl groups were not interacting with one another (Fig. 6) \[52\].

In the star-shaped hexa(ethynylferrocenyl)benzene \[14a\] (\(R = H\)), the three distinct two-electron waves observed in cyclic voltammetry essentially result from strong electrostatic interaction among redox centers in the presence of a perfluorinated tetraaryl borate electrolyte salt (Fig. 7) \[53\], a situation completely minimized (but strictly not totally absent) in dendrimers terminated by isolated redox-active termini \[54\].

In 1,2,3-triazolylbiferrocenyl-terminated dendrimers, however, the two ferrocenyl units of the biferrocenyl groups are interacting with each other, which allowed isolating class-II mixed-valent \[51\] Fe(II)–Fe(III) dendrimers such as \[13\] were isolated as well as the all-Fe(II) and all-Fe(III) dendritic complexes, although the ferrocenyl and pentamethylferrocenyl groups were not interacting with one another (Fig. 6) \[52\].
Moreover, in triazolylbiferrocenyl dendrimers the electron-withdrawing triazolyl linker renders the inner ferrocenyl group more difficult to oxidize than the terminal ferrocenyl group, thus oxo anions such as ATP are recognized by the latter, whereas metal cations such as Pd(II) interacting with the triazolyl ligands are recognized by the inner ferrocenyl group.

A related situation is encountered in arene-terminated dendrimers in which the two electronically interacting meta positions are functionalized by Lapinte-type piano-stool organoiron groups linked to the arene by an ethynyl group. In the latter case, the three oxidation states Fe(II), Fe(III) and the class-II mixed-valent Fe(II)–Fe(III) of the dendrimers were synthetically accessible. Such dendrimers were also synthesized with and without 1,2,3-triazolyl linkers, which allowed comparing the dendrimer stabilization of Au nanoparticles. The triazolyl ligand coordinated the Au(III) precursor intradendritically leading to the intradendritic stabilization. Moreover, the triazolyl ligand renders the inner ferrocenyl group more difficult to oxidize than the terminal ferrocenyl group.
formation of small Au nanoparticles whereas analogous dendrimers that do not contain triazolyl ligand interdendritically stabilize large Au nanoparticles outside the dendrimers [57].

Fig. 5. 27-Branch class-II mixed-valent triazolylbiferrocenyl-terminated dendrimer 12 synthesized by reaction of an azido terminated dendrimer with ethynylbiferrocene followed by stoichiometric oxidation using a ferricenium salt. The outer ferrocenyl groups are more easily oxidized than the inner ferrocenyl group because of the electron-withdrawing character of the 1,2,3-triazolyl linkers. Consequently, the outer ferrocenyl group recognize oxoanions such as ATP, whereas the inner ferrocenyl group recognize Pd2+ than coordinate to the triazole nitrogen atoms [55].

Fig. 6. Mixed-valent Fe(II)–Fe(III) dendritic ethynylferrocenyl complexes in which the ferrocenyl (in red) and pentamethylferricenium (in blue) centers have no significant electronic or electrostatic interaction [52]. (color online.)

Fig. 7. In hexa(ferrocenyldiylnyl)benzene 14a (R = H) and hexa (pentamethylferricenyl-ethynyl)benzene 14b (R = CH3), a single cyclic voltammetry (CV) wave is observed if [Nn-Bu4][PF6] is used as the supporting electrolyte indicating the absence of significant electronic interaction through the core, but three distinct CV wave are observed (R = H) with [Nn-Bu4][BARF4] (ArF = 3,5-C6H3(CF3)2) due only to the electrostatic interactions between the neighboring ferricenium groups [53,54]. With R = CH3, shielding of this electrostatic effect by the methyl substituents provokes the appearance of a broad multi-electron wave with the latter electrolyte.

7. Conclusion and prospect

Sophisticated organoiron engineering results in both remarkable ligand activation modes (Schemes 1–3) and redox flexibility. These properties involve a minimized structural transformation that is characteristic of late first-row transition-metal complexes with π ligands (Fig. 1) [58]. Such designs result in unique physical properties together with robustness of the complexes under various oxidation states including mixed-valences. These mixed-valent
dendrimers can result, in giant ferrocenyl dendrimers terminated by a large number of redox groups (Fig. 2 and Fig. 3), from statistical distribution of the two oxidation states (Fig. 5), slightly different structure upon introducing methyl groups on a Cp ligand in the absence of inter-site interaction (Fig. 6), and linkage to the core de-symmetrizing the two electronically interacting redox centers, or using electronically interacting centers (Fig. 4). Interactions between two redox centers in arene-cored structures can be not only electronic (Fig. 8), but also electrostatic, and sometimes such as in hexa(ferrocenylethynyl)benzene it is possible to isolate the electrostatic interaction, when the electronic interaction is not significant (Fig. 7). These concepts have applications in nanosciences [59] and nanomaterials chemistry of metal-containing macromolecules [60,61] including transition-metal nanoparticles that are of interest in catalysis [19], sensing [24] and nanomedicine [20,59].

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