ChemPubSoc Europe

DOI: 10.1002/ejic.201600983

EurJIC European Journal of Inorganic Chemistry

Microreview

Ferrocenes

# Why is Ferrocene so Exceptional?

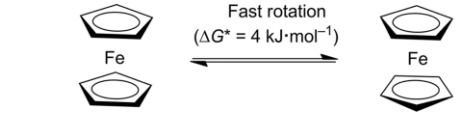
Didier Astruc*[a]

*Dedicated to Professor Henri B. Kagan at the occasion of his 85th birthday*

**Abstract:** The appearance of ferrocene in the middle of the 20th century has revolutionized organometallic chemistry and is now providing applications in areas as varied and sometimes initially unexpected as optical and redox devices, battery and other materials, sensing, catalysis, including asymmetric and enantioselective catalysis, and medicine. The author presents here a general, although personal, view of ferrocene's chemistry, properties, functions, and applications through a literature survey involving both historical and up-to-date trends and including examples of his group's research in a number of these areas. The review gathers together general features of ferrocene chemistry and representative examples of the salient aspects. Its focus is on ferrocene's basic properties, ferrocene-containing ligands, the ferrocene/ferricinium redox couple, ferrocene mixed-valence and average-valence systems, the ferricinium/ferrocene redox shuttle in catalysis, ligand-exchange reactions, ferrocene-containing polymers, ferrocene-containing structures for cathodic battery and other materials, ferrocenes in supramolecular ensembles, liquid crystals, and nonlinear optical materials, ferrocene-containing stars and their electrostatic effects, ferrocene-containing dendrons, dendrimers, and nanoparticles (NPs) and their application in redox sensing and catalysis, and ferrocenes in nanomedicine.

## Introduction – Ferrocene's Basic Properties

The process technicians who noticed the formation of an orange sludge when they inspected pipes used in the manufacture of cyclopentadiene upon cracking dicyclopentadiene at Union Carbide in the late 1940s did not imagine that only a few years later the new compound involved would be the subject of wonder from the entire chemistry community. The first publications, submitted in 1951, ignored Langmuir's[1] and Sidgwick's[2] 18-electron (18e) rule and represented the compound with two monohapto cyclopentadienyl ligands, as $[Fe(\eta^1\text{-}C_5H_5)]_2$.[3,4] The real sandwich structure – $[Fe(\eta^5\text{-}C_5H_5)]_2$ – was disclosed and published in 1952 by Wilkinson, Rosenblum, Whiting, and Woodward[5] in Harvard and by Fischer and Pfab[6] in Munich. It has a $D_{5h}$ (eclipsed) or $D_{5d}$ (staggered) conformation and a very small rotation energy barrier [Equation (1)].




(1)

This structure immediately appeared all the more fascinating, because nobody had seen anything like that, and especially because ferrocene (FcH) – the name coined by Woodward and Whitting[7] – appeared to possess three types of exceptional properties:

(i) stability up to 400 °C (m.p. 172.5 °C) with an iron center that has the saturated electronic structure of krypton,

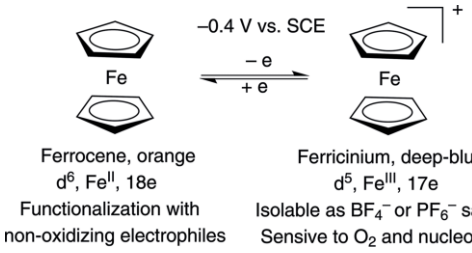
(ii) reactivity as a superaromatic electrophile,[7] and

(iii) mild and reversible oxidation around +0.4 V versus saturated calomel electrode (SCE) [Equation (2)].

These properties, in addition to good solubility in all common organic solvents and stability in air, together with the resulting enormous number of ferrocene derivatives and ferrocene-containing materials synthesized in the last 65 years, have

[a] *ISM, UMR CNRS 5255, Univ. Bordeaux, 33405 Talence Cedex, France*
*E-mail: didier.astruc@u-bordeaux.fr*
*http://astruc.didier.free.fr/cv-fr.htm*
*ORCID(s) from the author(s) for this article is/are available on the WWW under http://dx.doi.org/10.1002/ejic.201600983.*

*Didier Astruc studied and passed his Ph.D. in Rennes with Professor René Dabard, did postdoctoral work with Professor Richard Schrock at MIT, and is Professor of Chemistry at the University of Bordeaux and Member of the Institut Universitaire de France. His interests are in organometallic electronics and in nanoreactors for catalysis, sensing, and nanomedicine.*



(2)

made ferrocene an icon in organometallic chemistry. Ferrocenes have been the subject of more than 18000 publications so far (Web of Science), with numbers of publications appearing yearly still increasing (for books on ferrocenes, see refs.[8–11], and for historical surveys, see refs.[12–18]).

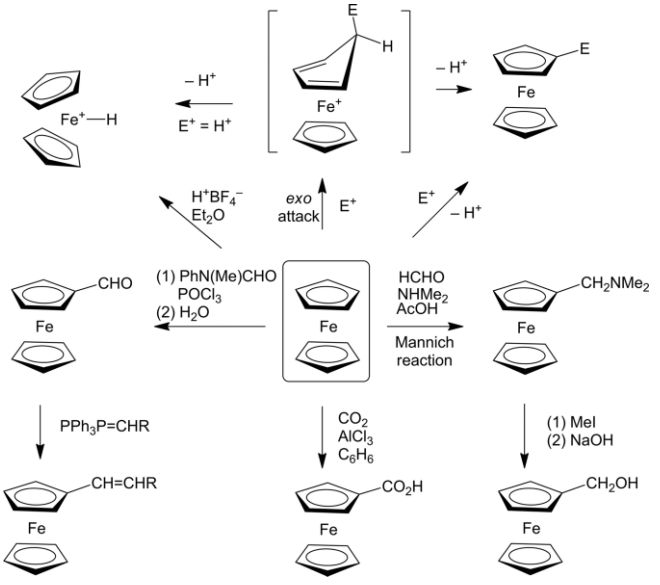
Imitating the most common synthesis of ferrocene – from iron chloride and cyclopentadienylsodium [Equation (3)] – the reactions between cyclopentadienyl salts and all transition metals provided early on an easy route to transition-metal sandwich complexes with parallel rings for late transition metals and main-group metals and bent structures for early transition metals, with additional equatorial ligands.[12,16]

$$FeCl_2 + 2\ NaCp \rightarrow FeCp_2 + 2\ NaCl\ (in\ THF) \quad (3)$$

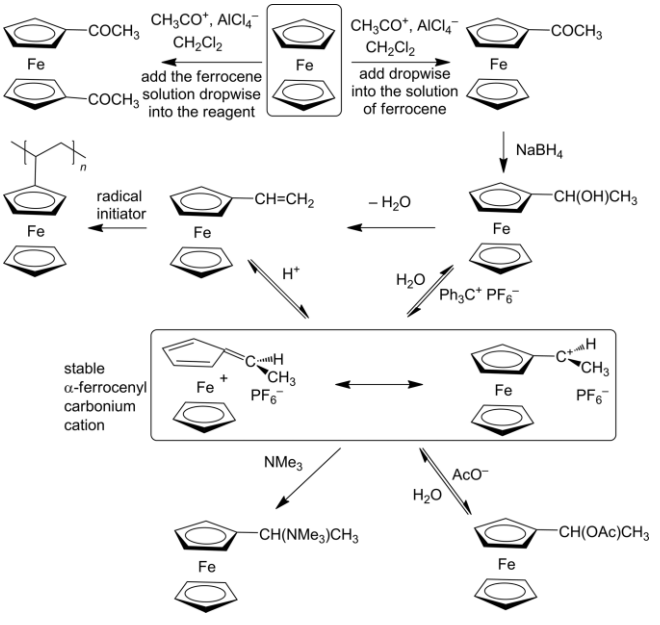
The robustness of ferrocene, like that of its lower-row analogues ruthenocene and osmocene,[8,12] is the result of the 18e count of its central metal atom, contrasting with neighboring late-transition-metal neutral metallocenes, which have the odd-number-electron structures of $d^5$ 17e for manganocene and $d^7$ 19e for cobaltocene.[12] Robust isoelectronic 18e ferrocene-type structures are evident in the forms of the decamethylmanganocene anion,[19] a strong reductant, and cobalticinium cation,[20] which, with cobaltocene, forms $[Co^{III}Cp_2]^+/Co^{II}Cp_2$, another useful and complementary redox couple.[21]

The large family of substituted cyclopentadienyl ligands[22] has enriched the ferrocene family with a great variety of ferrocene derivatives produced by treatment with $Fe^{II}$ salts [as in Equation (3)], adding to the many ferrocene derivatives accessible through electrophilic reactions with ferrocene itself (Scheme 1).

Strong acids protonate the iron center, yielding the cationic iron(IV) hydride complex $[Fe(H)Cp_2]^+$, but the most classic and useful representative electrophilic reaction of ferrocene is its acylation in the presence of acyl chlorides and $AlCl_3$.[4,23] For instance, with acetyl chloride, the reaction is currently used in undergraduate schools to show the difference in reactivity between the two ferrocene rings, with the first acetylation completely deactivating the acetylated ring, but also sufficiently deactivating the unsubstituted ring to slow down its acylation.[24,25] In this way, the monoacetylation is selective if it is carefully controlled. The red product acetylferrocene is easily separated from minor amounts of yellow-orange unreacted ferrocene and of deep red 1,1′-diacetyl ferrocene by column chromatography on alumina or silica. The acetylation of both rings to yield 1,1′-diacetylferrocene is also easily conducted by slowly adding ferrocene to a dichloromethane solution of 2 equiv. of the acetylation reagent $CH_3CO^+/AlCl_4^-$ (Scheme 2).

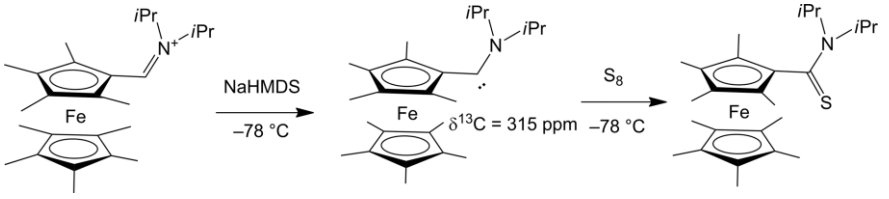



Scheme 1. Representative electrophilic reactions with ferrocene and subsequent chemistry (together with acylation, Scheme 2) and mechanism (top).

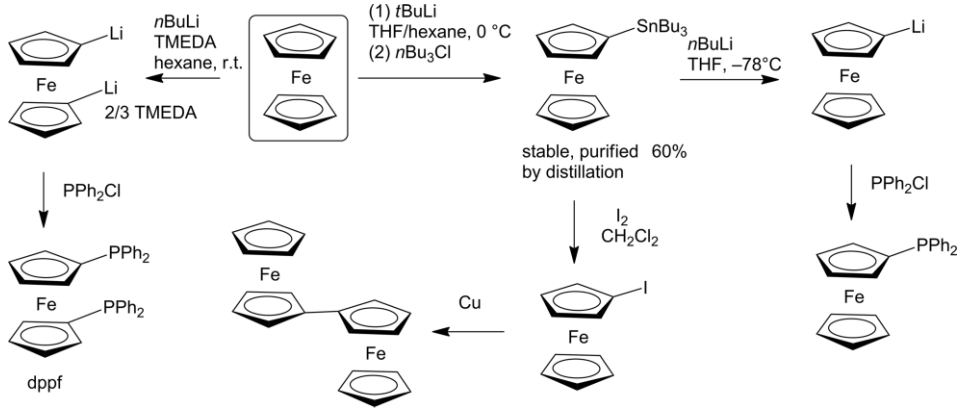



Scheme 2. Acetylation of ferrocene and key subsequent chemistry.

Reduction of acetylferrocene with $NaBH_4$ gives the secondary alcohol $FcCHOHCH_3$,[26] and the resolution of the two formed enantiomers[27] with the aid of a chiral HPLC column is another valuable undergraduate laboratory experiment.[28,29] $FcCHOHCH_3$ can also be dehydrated to give vinylferrocene.[30–32] Treatment of alcohols FcCHOHR with $[Ph_3C]^+[PF_6^-]$ or hydrolysis of acetates FcCH(OAc)R yields the stabilized α-ferrocenylcarbonium ions $[FcCHR]^+$ that are isolable as $BF_4^-$ or $PF_6^-$ salts.[33] These cations are also accessible by 1e oxidation of vinylferrocenes[34] and can be regarded as distorted cationic $\eta^6$-fulvene complexes (Scheme 2) isolobal to $[FeCp(\eta^6\text{-arene})]^+$ (Cp = $\eta^5$-cyclopentadienyl) with a slight shift of the iron center towards the exocyclic carbocation (vide supra).[35] Deprotonation of the α-ferrocenylcarbonium salts would yield α-ferrocen-




Scheme 3. Bertrand's characterization of an α-ferrocenylcarbene.[37]



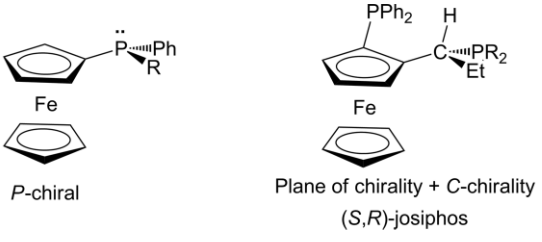

Scheme 4. Clean mono- and dilithiation of ferrocene and relevant chemistry.

ylcarbenes,[36] but the ferrocenyl substituent does not electronically stabilize carbenes, and spectroscopic characterization of these species (that dimerize to olefins) remained elusive until it was recently achieved by $^{13}C$ NMR spectroscopy ($\delta_{carbene\ C}$ = 315 ppm) by Bertrand's group with the aid of an N(*i*Pr)$_2$ substituent and trapping with $S_8$ to give the thioketone (Scheme 3).[37]

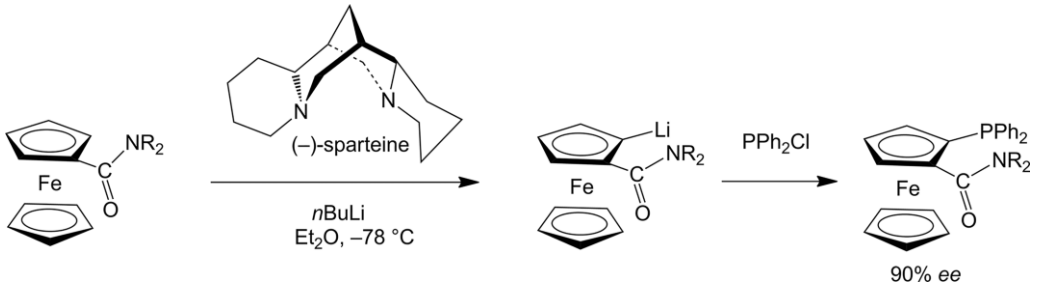
The direct lithiation of ferrocene with butyllithium is another key reaction yielding 1,1′-dilithioferrocene,[38] but monolithiation that is marred by the generation of some 1,1′-dithiated product. A smart and convenient method was, however, reported by Kagan's group, who used the high-yielding formation of pure (tri-*n*-butylstannyl)ferrocene, which is a convenient precursor of pure lithioferrocene[39] and many other monofunctional ferrocene derivatives, and in particular to very useful ligands (Scheme 4).[40]

## Ferrocene-Containing Ligands

The extremely rich reactivity of ferrocene has allowed the synthesis of very useful and currently widely utilized ligands,[40–55] especially a large variety of ferrocenylphosphines that are accessible either from lithioferrocene and 1,1′-dilithioferrocene (Scheme 4) or through direct Friedel–Crafts reactions with ferrocene in the presence of aluminum chloride.[9] The achiral diphosphine 1,1′-bis(diphenylphosphino)ferrocene (dppf) is especially widely used in catalysis; in particular, its palladium complex [Pd$^{II}$Cl$_2$(dppf)][56] is used for palladium-coupling reactions with industrial applications in pharmaceuticals and agrochemistry. Ferrocenyl-substituted monophosphines are *P*-chiral when the two other P-substituents are different, and such phosphines P(Fc)(R)(Ar) have been used in asymmetric catalysis. Chiral ferrocenyl-based ligands are numerous and useful in enantioselective syntheses.[9,57,58]



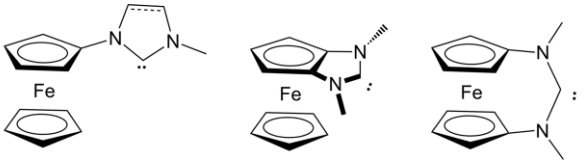

When two substituents on a ferrocene ring are different, the ferrocene derivative has a plane of chirality (below). The synthesis of relevant phosphines starts from a monofunctional ferro-




Scheme 5. Enantioselective synthesis of a chiral phosphine involving the ferrocenyl plane of chirality. See Strohmann et al.[357]

cene derivative and uses a chiral diamine and butyllithium. The diamine chelates the Li cation, rendering the reagent monomeric, and thus more reactive, and polarizes the Li–C bond, which enhances the reactivity of the butyllithium (Scheme 5).

Many bidentate ligands in which the ferrocene unit bridges a phosphine and another heteroatom ligand have been designed. For instance, Hor's group reported nickel(0) complexation by hemilabile *P,N*-ferrocene ligands and demonstrated their ethylene oligomerization activities.[59,60] Through the use of other chelates such as *N,S* ligands, ferrocene has been incorporated – by the Lopez group, for instance – onto palladacycles.[61] Key ligands that are most useful for stabilizing gold and palladium NPs are ferrocene- and biferrocene-containing thiolates, and these ligands also serve as self-assembled monolayers.[62–66] The Bilstein group has designed N-heterocyclic carbenes (NHCs) containing a ferrocenyl substituent (or substituents) on the nitrogen atom(s) and has synthesized *N,N'*-diferrocenyl heterocycles.[67]




Ferrocenyl *N*-heterocyclic carbenes

## The Ferrocene/Ferricinium Redox Couple

Mild oxidation of ferrocene by, for instance, iodine, $FeCl_3$, or $AgNO_3$, etc. yields a stable blue ferricinium salt that can be reduced back to ferrocene with, for instance, an acidic aqueous solution of $TiCl_3$ or thiosulfate or by other mild reductants such as decamethylferrocene. $HAu^{III}Cl_4$ in water is reduced by ferrocene in diethyl ether solution (within seconds on stirring at room temperature) to afford air-stable ferricinium chloride protected gold NPs (Figure 1).[69]

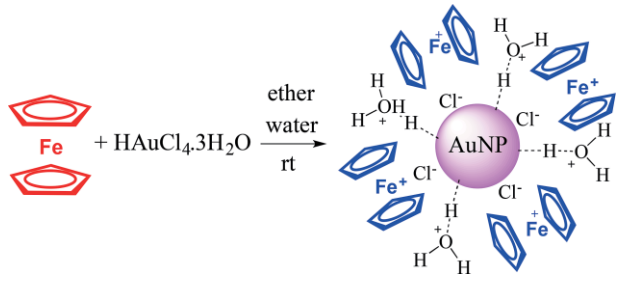



Figure 1. Fast and simple formation of ferricinium chloride stabilized gold NPs under ambient conditions through the biphasic reaction between ferrocene in diethyl ether and aq. $HAu^{III}Cl_4$.[69]

Ferricinium salts (most commonly the $PF_6^-$ salt) are mild 1e oxidants that are especially useful in organometallic and inorganic chemistry.[21,68] Other names for ferricinium include ferrocenium and ferricenium; they have also been used since the early days. Because "ferro" is conventionally used for $Fe^{II}$ complexes and "ferri" for $Fe^{III}$ complexes, it would be best to use the name ferricenium or ferricinium, especially because, in addition, the name ferrocenium hydride should be reserved for the protonated form of ferrocene $[Fe(H)(\eta^5\text{-}C_5H_5)_2]^+[PF_6^-]$, a "bent" metallocene hydride.[70,71]

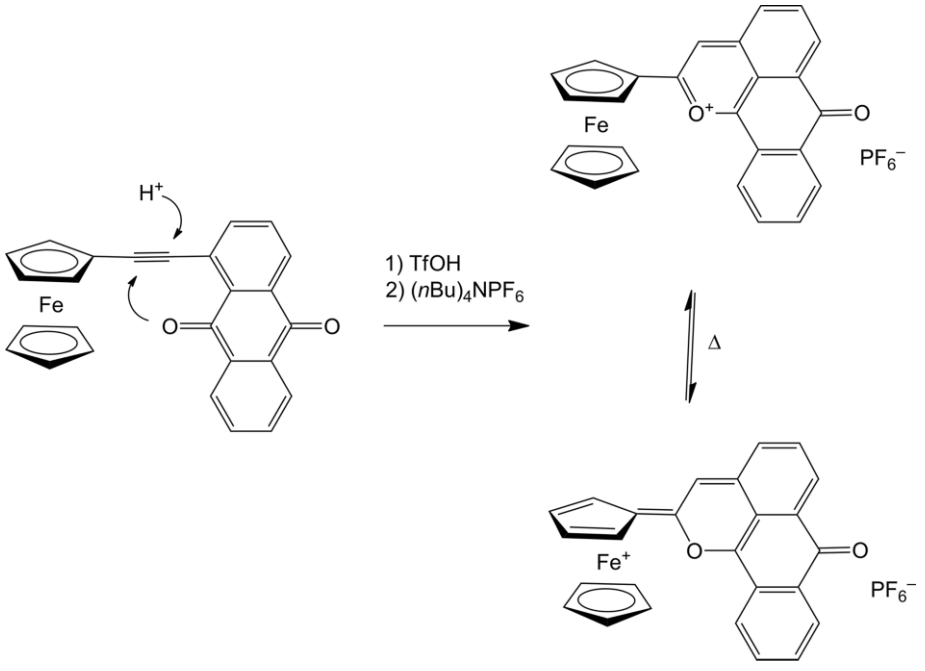
In cyclic voltammetry a chemically and electrochemically reversible single-electron (1e) redox wave is found upon anodic oxidation around 0.4 V versus SCE,[68] but the exact redox-potential value depends on the solvent, because of the variable interactions of the different solvents with the positively charged central iron. Although ferrocene has long been considered a reference for the measure of redox potentials, decamethylferrocene and other permethylated metallocenes are therefore much more reliable references, because in these cases the central metal atom is protected from these interactions by the cage of ring methyl groups, and the redox potential is then independent of the nature of the solvent.[72,73]

The electrochemical reversibility signifies that electron transfer from the ferrocene to the anode and back-electron transfer between the anode and ferricinium are fast on the timescale of potential scanning in cyclic voltammetry. This high heterogeneous electron-transfer rate is due to the fact that the structures of ferrocene and ferricinium are almost exactly the same (no bond is broken during the redox process), with Fe–C bond lengthening upon single-electron oxidation of ferrocene being only of the order of 0.1 Å.[74–77] Electron transfer from ferrocene to acceptors of interest such as DNA has been studied from the kinetic viewpoint by Kraatz's group.[78] This fast electron transfer rate and easy ferrocene oxidation are having far-reaching consequences and applications in medicine, redox sensing, redox catalysis, and materials science, including in batteries, electrochromics, etc. (vide infra). For instance, ferrocene-containing nanostructures such as ferrocene–peptide conjugates undergo extensive rearrangements upon oxidation of the ferrocene unit to ferricinium, as recently shown by Kraatz's group.[79] Although they are relatively stable in this solid state, ferricinium salts are air-sensitive and react with $O_2$ in organic solutions,[80] which slightly limits their applications, unless at least one ring is permethylated.

The Nishihara group discovered a counter-anion-dependent and thermally modulated valence tautomerization of ferrocenyl-conjugated pyrylium salts formed by strong-acid-mediated cyclocondensation of 1-(ferrocenylethynyl)anthraquinone yielding 2-ferrocenyl-7-oxodihydrodibenzochromenylium salts [Equation (4).[81]

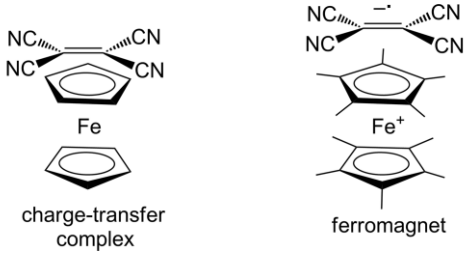
This taumerization, in which the cationic iron sandwich form is favored at high temperatures for the $PF_6^-$ salt, was not observed for the $BF_4^-$ counterpart, due to increased coulombic attraction between this smaller counter-anion and the localized oxonium charge. This situation is somewhat reminiscent of that of α-ferrocenylcarbonium (vide supra).[81] Along similar lines, this research group also reported remarkable ferrocene–dithiolene hybrids that display temperature-gated proton-coupled electron transfer[354] or reversed intramolecular charge transfer[355] in which the redox properties of ferrocene play a main role.

Permethylmetallocene cations are considerably more stable than their parent metallocenes, due to the stereoelectronic protection by the methyl ring substituents, and this applies, for




(4)

instance, to pentamethylferricinium and decamethylferricinium. Decamethylferrocene[82] is more easily oxidized than ferrocene by 0.5 V. For instance, whereas ferrocene does not reduce tetracyanoethylene (TCNE), Miller's and Epstein's groups reported the first molecular ferromagnet $[Fe(\eta^5\text{-}C_5Me_5)_2]^+[TCNE]^{-\bullet}$ upon oxidizing decamethylferrocene with TCNE.[83]

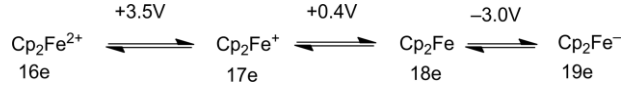



The stronger reducing power of permethylferrocenes in relation to ferrocene has recently been used, for instance, by the Fukusumi group with octamethylferrocene for two-electron oxygen reduction with $Cr^{V}$[84] or $Mn^{V}$ corrole[85] derivatives.

Ferrocene-based liquid crystals can be profoundly affected by redox change. For instance, oxidation of a non-mesomorphic persubstituted ferrocene derivative leads to the corresponding ferricinium species, which exhibits a smectic A phase.[86]

Beer's group demonstrated that the photophysical properties of a d-f dyad were reversibly switched by oxidizing the ferrocene chromophore to ferricinium.[87] A remarkable ferrocene storage method in dendrimers was reported by the Yamamoto and the Nishihara groups in the form of Yamamoto's polyphenylazomethine dendrimers that were able to encapsulate ferricinium units through complexation of the electron-donating skeleton of the polyphenylazomethine dendritic imines. By utilizing the redox properties of ferrocene, the authors achieved electrochemical control over the encapsulation and release of ferrocene into the dendrimers in the same way as redox-responsive proteins such as ferritin.[88] The chemically or physically (adsorption) based modification of electrodes[89] with ferrocene derivatives as redox relays or redox catalysts has long been of considerable use in electrochemical sensing (vide infra). For instance, electrically insulating proteins can be made redox-conducting,[90] electrode-coated monolayers can mimic photosynthetic energy and electron transfer,[91] and single-base mismatches in DNA can be electronically detected.[92–94]

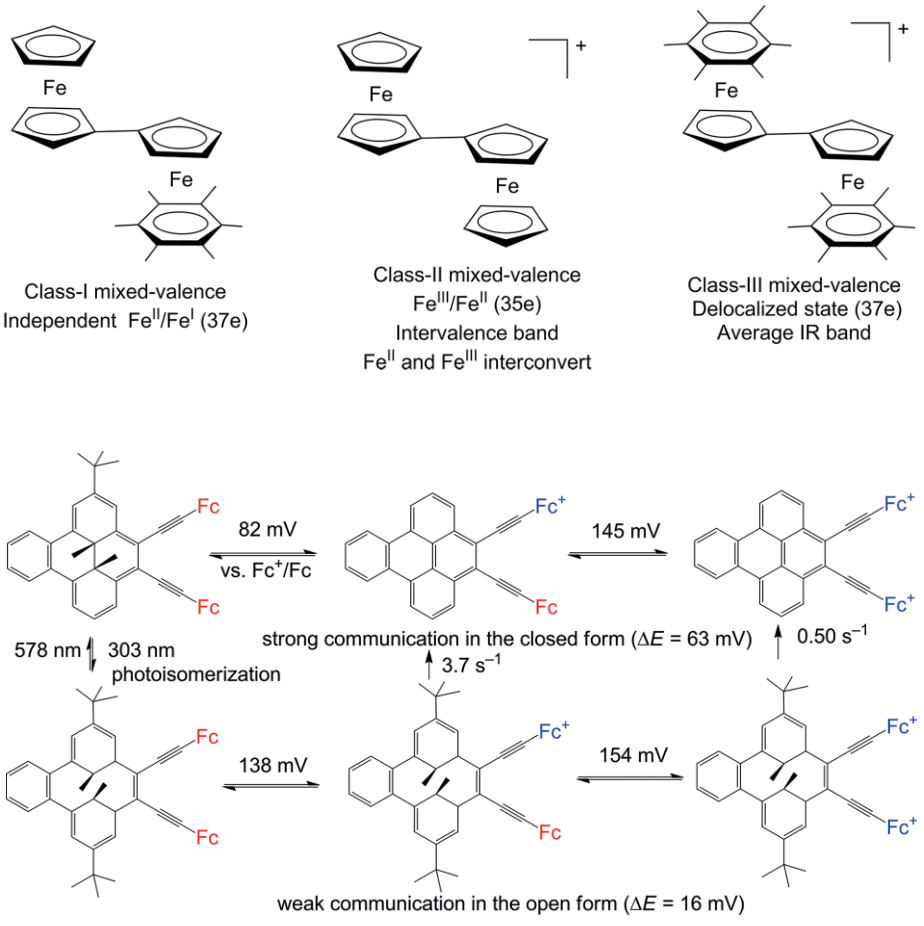
Finally, the other oxidation states – $Fe^{IV}$ and $Fe^{I}$ – of ferrocene have been reversibly electrochemically generated, but the potentials are so extreme that these very reactive species could not so far be observed spectroscopically (Scheme 6). In cationic iron sandwich complexes isolobal to ferrocene, the isolation of such $Fe^{I}$ complexes is possible, however (vide infra).




Scheme 6. Electrochemical sequences of reversible 1e redox reactions of ferrocene.[74]

## Ferrocene Mixed-Valence and Average-Valence Systems

In 1970, single-electron oxidation of biferrocene was reported to provide one of the first mixed-valence system for which the infrared spectrum (i.e., at a spectroscopy frequency of about $10^{13}$ $s^{-1}$) showed the signals of both $Fe^{II}$ and $Fe^{III}$, indicating localized class-II mixed valency in the Robin–Day classification,[95–99] whereas in the related dinuclear complexes $[Fe_2(\mu_2,\eta^{10}\text{-fulvalene})(\eta^6\text{-}C_6H_6)]^+[PF_6]^-$ and $[Fe_2(\mu_2,\eta^{12}\text{-biphenyl})Cp_2]^+[PF_6]^-$ intermediate the infrared band indicated average class-III mixed valency.[100–102] Mössbauer spectra (i.e., at the frequency of about $10^7$ $s^{-1}$) of biferrocenium derivatives are interesting, because, depending on the nature of Cp substituents




Scheme 7. Nishihara's electronic communication in bis(ferrocenylethynyl)polyaromatics modulated by photochemically driven ring closing.[120]

and counter anions, localized or delocalized mixed valency is observed.[102]

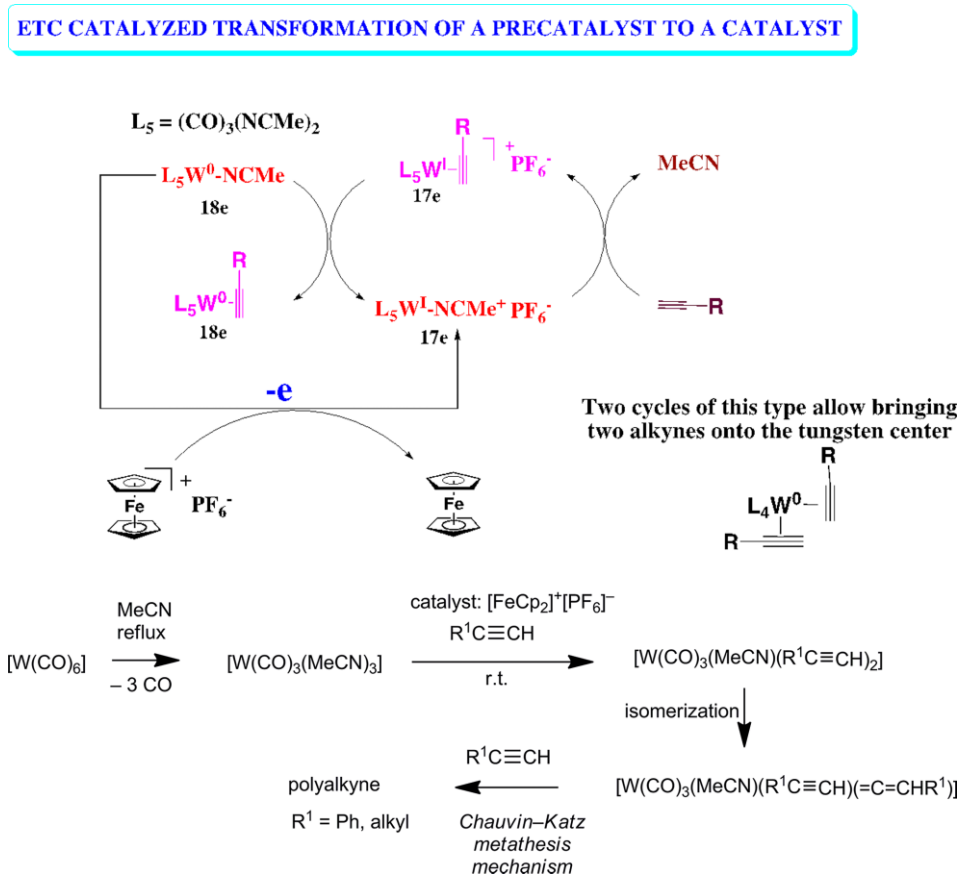
Ferrocene units have been useful for the study of electronic communication through bridges with greater or lesser degrees of electronic conductivity. For instance, studies conducted by Lang et al.[103–110] in particular have scrutinized electronically intercommunicating iron centers in di- and tetraferrocenylpyrroles and other heterocycles. Diethynylbiferrocene has been used by the Lapinte and Lang groups as a bridge between several redox-active group 8 metal fragments in order to examine the nature of the electronic communication between these groups with absorption and vibrational spectroscopy of the mixed valences, and the interaction was shown to be weak but measurable.[111]

The Nishihara group synthesized azo-bridged ferrocene oligomers and a polymer and conducted electrochemical and optical analyses of internuclear electronic interactions in the mixed-valence states. The redox potentials and intervalence band characteristics were shown to depend significantly on the solvent. The solvent effect of the intervalence band on $\nu$(max) cannot be interpreted only in terms of the parameters in the Marcus–Hush theory, thus indicating that the nature of the solvent as donor or acceptor needs to be taken into account in the electron-exchange process in the mixed-valent states.[112–117] Visible-light photochromism of Sakamoto's and Nishihara's related mixed-valent bis(ferrocenylethynyl)ethenes switches electronic communication between the ferrocene sites.[114,118] Structural conversion and spin separation in bis(ferrocenylethynyl)anthraquinones were also triggered by Nishihara's group upon proton-coupled intramolecular electron transfer.[119] This research group reported redox-assisted ring closure of the photogenerated cyclophanediene form of diferrocenyldimethyldihydropyrene with interferrocene electronic communication switching. Reversible high-yielding photoisomerization was found to take place between the closed dimethyldihydropyrene form and the open cyclophanediene form upon alternate irradiation with visible (578 nm) light and UV (303 nm) light (Scheme 7).[120]

Kaim's charge delocalization in heterodimetallic systems containing ferrocene has been examined by IR and UV/Vis spectroscopy and involves some, usually low, charge transfer.[121,122]

## The Ferricinium/Ferrocene Redox Shuttle in Catalysis

Switching between ferrocene and ferricinium in a device often has dramatic consequences for the outcome of a catalytic reaction. Several examples highlight this trend below. Ferricenium hexafluorophosphate serves as an electron-transfer-chain cata-




Scheme 8. Proposed mechanism for the remarkable acceleration by the electron-transfer-chain (ETC) catalyst (ferricinium) of the metathesis polymerization of terminal alkynes.[123]

lyst for carrying out ligand substitution of MeCN in $[W(CO)_3(MeCN)_3]$ by terminal alkynes, thus acting as a precatalyst for the polymerization of these terminal alkynes.[123] The mechanism combines the electrocatalytic exchange of the acetonitrile ligand on tungsten for alkyne ligands[124] with polymerization by metathesis of the terminal alkynes catalyzed by W–vinylidene species.[125] In this Chauvin–Katz mechanism,[125,126] coordination of the terminal alkyne on the W–vinylidene species after rearrangement of a W($\eta^2$-alkyne) species produces a tungstacyclobutene. The ferricinium electrocatalyst[127] accelerates the replacement of acetonitrile by the alkyne ligand via odd-number-electron W species by several orders of magnitude. Polymerization occurs immediately under ambient conditions in the presence of the ferricenium electrocatalyst instead of proceeding at 100 °C over several hours in its absence (Scheme 8).[125]

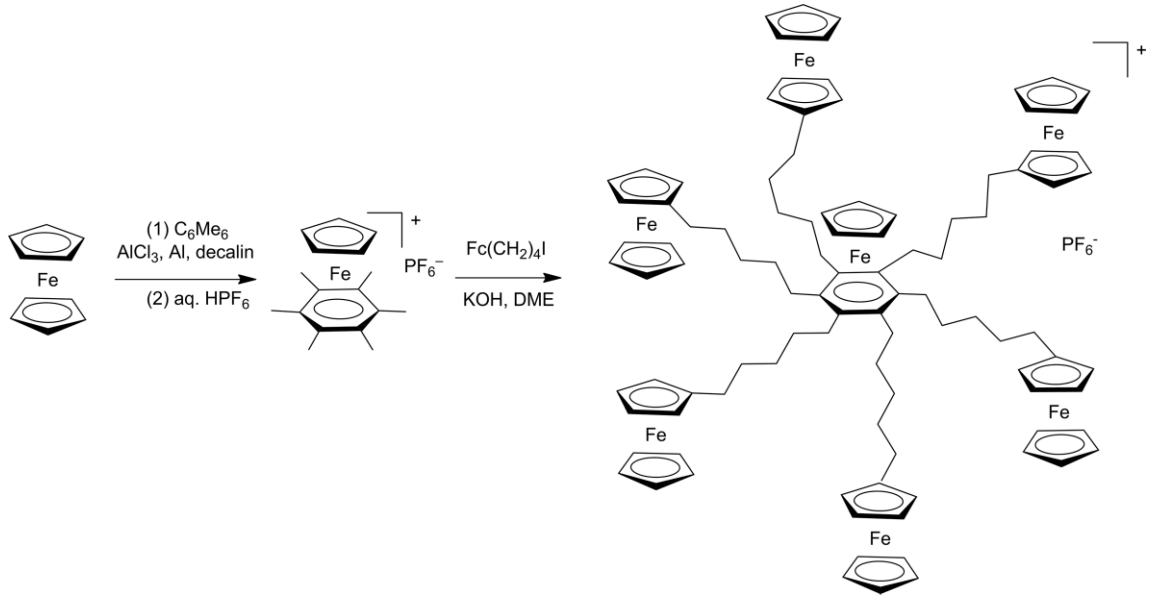
Studer and Curran recently published an excellent review article entitled "The electron is a catalyst" that gives examples of how electron shuttles are used catalytically in organic chemistry.[128] Related concepts were pioneered by Savéant,[129] Russell,[130] Bunnett,[131] and Kornblum ($S_{RN}1$),[132] and electron-transfer reagents such as $Ar_3N^{+\cdot}$ in oxidation and naphthylsodium or photocatalysts in reduction require more energy (more extreme redox potentials) than in inorganic and organometallic systems,[133] for which similar concepts had been examined by Taube in the early 1950s[134] and later by Kochi.[124] A recent example, however, uses the ferricinium/ferrocene shuttle in organic chemistry as follows. Ferrocene was used as an electron-shuttle catalyst in C–H imidation of heteroarenes. The decomposition of a perester reagent yielded a succinimidyl radical that added to an aromatic system. In this way, the C–H imidation used a new perester-based self-immolating reagent. Succinimide products obtained were deprotected in situ, giving the corresponding anilines.[135]

The ferricinium/ferrocene redox shuttle was also shown by Plenio's group to trigger ring-opening metathesis polymerization (ROMP) catalyzed by a second-generation Ru–benzylidene Grubbs catalyst attached both to silica NPs through a functional NHC ligand and at the same time to a poly(vinylferrocene) polymer. In the oxidized ferricinium form of the polymer the ROMP reaction was inhibited, but not in the reduced ferrocene form.[136] Likewise, it was shown that upon single-electron oxidation, (ferrocenylphosphine)Ru complexes lose some of their catalytic activity for the isomerization of the allylic alcohol oct-1-en-3-ol, due to reduced electron density on the Ru center.[137]

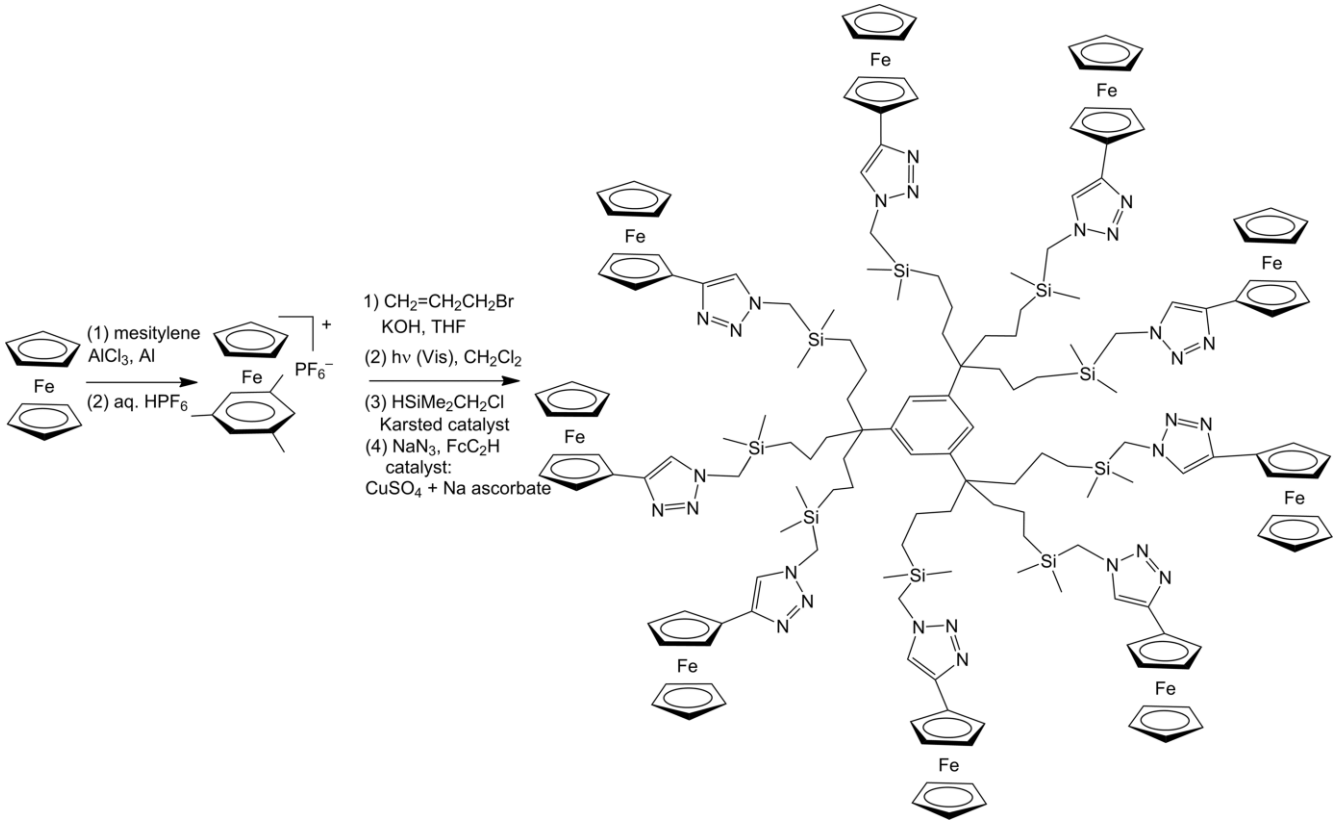
## Ligand-Exchange Reactions and Related Iron Sandwich Complexes

Although the best-known reactions of ferrocene are its electrophilic reactions and its reversible 1e oxidation to ferricinium,

ligand-exchange reactions are also a rich and synthetically very useful source of ferrocene-containing macromolecules and nanomaterials. The Nesmeyanov group showed that exchange of a single ferrocene ring for an aromatic group was easily carried out in the presence of a strong Lewis acid such as $AlCl_3$ to produce a salt of the robust cation $[FeCp(\eta^6\text{-arene})]^+$.[138,139] This has a rich reactivity with nucleophiles, reducing agents, and bases[140,141] that resembles that of the cobalticinium salts.[142,143] The most remarkable reactions of these cationic iron sandwich complexes are their very useful peralkylation and perallylation reactions with alkyl iodides and allyl bromide, respectively, in the presence of KOH or *t*BuOK under ambient conditions, leading to metallostars (Scheme 9) and metallodendrimers (Scheme 10).[144,145]

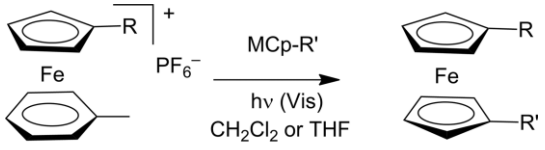



Scheme 9. $CpFe^+$-induced hexaferrocenylalkylation of the hexamethylbenzene ligand.[145]




Scheme 10. Synthesis of a ferrocene-terminated dendrimer based on the $CpFe^+$-induced nonaallylation of mesitylene.[144,300]

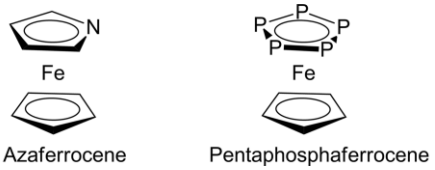
The metallodendrimers in particular can be further involved in a variety of transformation reactions that provide a rich chemistry. Another useful aspect of the $[FeCp(\eta^6\text{-arene})]^+$ salts is their iron-based redox chemistry.[141,146] Whereas ferricinium salts are mild oxidants, the isolobal 17e sandwich complex $[Fe(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Me_6)]^{2+}[SbCl_6]^{2-}$ is a strong oxidant,[146] and the 19e complexes $[FeCp(\eta^6\text{-arene})]$ are strong reductants.[147,148] With the 18e monocations, these 17e and 19e Fe sandwich complexes form other useful robust redox couples with very positive and very negative redox potentials, respectively.[149,150] The reduced $Fe^I$ forms are even stronger reductants than cobaltocene[151,152] and were designed as electron reservoirs paralleling fullerenes.[153] Other practical reactions involve the visible-light photolytic cleavage of the Fe–arene bond in $[FeCp(\eta^6\text{-arene})]^+$ salts, leading to functional ferrocenes [Equation (5)] and other organoiron cations,[154–157] whereas thermal arene exchange in these neutral 19-electron complexes proceeded at sub-ambient temperature.[158]




R = H, Cl, COMe, $CO_2Me$, $CO_2CH_2CCH$, $NHCH_2Ph$
R' = $CO_2Me$, $PPh_2$, $SiMe_2CH_2Cl$
M = Li or Na (5)

With 1,1′-diacetylferrocene, only double ring exchange with polymethylbenzene derivatives was achieved, yielding $[Fe(arene)_2]^{2+}$ salts, a series of complexes isolobal to ferrocene with rich redox and arene activation properties.[159,160]

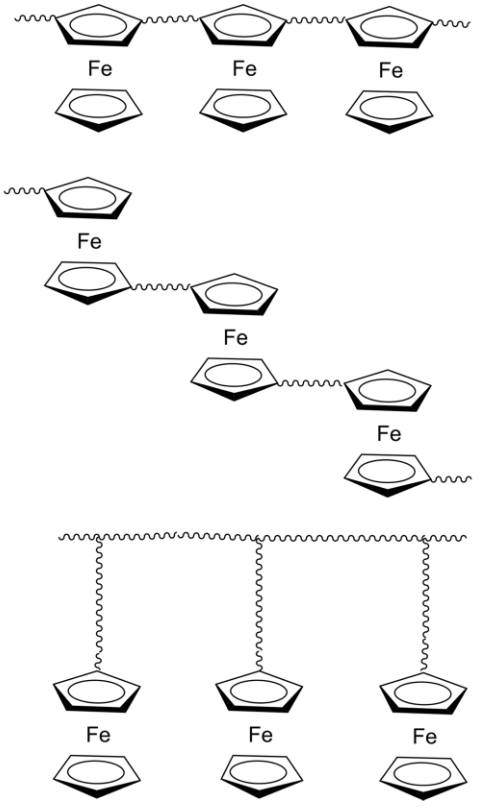
Carbon atoms in one ferrocene ring can also be replaced by heteroatoms, although access does not involve ferrocene. For instance the piano-stool complex $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-pyrrole})]$ is used as a precursor for the synthesis of azaferrocene, $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_4N)]$,[161] whereas pentaphosphaferrocene, $[Fe(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}P_5)]$, was synthesized by a related strategy[162] that has been extended to a large variety of sandwich-type complexes containing the CpFe fragment and to their supramolecular applications.[163–166]




## Ferrocene-Containing Polymers

Since the first report, by Arimoto and Haven in 1955, of the homo- and copolymerization of vinylferrocene derivatives,[167] ferrocene polymers have remained a continually blossoming field, with more than 2000 publications that have appeared up to now and applications in biomedicine, electrocatalysis, membrane fuel cells, sensors, self-healing materials, plastics, batteries, aerospace materials, liquid crystals, photovoltaic cells, and nonlinear optics.[168–172]

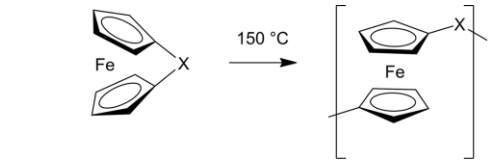
Ferrocene-containing polymers can contain the ferrocene units either in the main polymer chain or in the polymer side chains.




In the first category, polymerization is based on various polycondensation reactions of 1,2-, 1,3-, or 1,1′-disubstituted ferrocenes with or without spacers, whereas in the second category, only monosubstituted ferrocenes are needed. Biferrocenes that are functionalized on the free Cp rings are also practical units for the polycondensation reactions and lead to multi-functional polymers with properties useful for applications in mixed valency, solubility control, electrochromics, sensing, and catalysis.

The most remarkable type of formation of ferrocene polymers containing ferrocene units in the main chain is the ring-opening polymerization (ROP) of strained ring-tilted ferrocenophanes first reported by Manners and co-workers in 1992,[173,174] and then developed and extended extensively by the same group with a number of useful applications [Equation (6)]. For ROP, the strained bond in a ferrocenophane is broken in a number of ways, including in thermal, anionic, cationic, photolytic, and transition-metal-catalyzed polymerization, on which the molecular weights and architectures depend.[174–176]

The molecular weight of the polymers, as well as their architecture and living character, depend on the mechanism, however. Living polymerization was found to be photocontrolled.[175] In addition, this method proved so rich and powerful that it was subsequently also applied to a large variety of non-ferrocene transition-metal sandwich derivatives. The electrochemical analysis of polymers such as $[Fe(\eta^5\text{-}C_5H_4)_2SiMe_2]_n$




Manner's ring-opening polymerization of strained ferrocenophanes
Prototypical example: X = $SiMe_2$


(6)

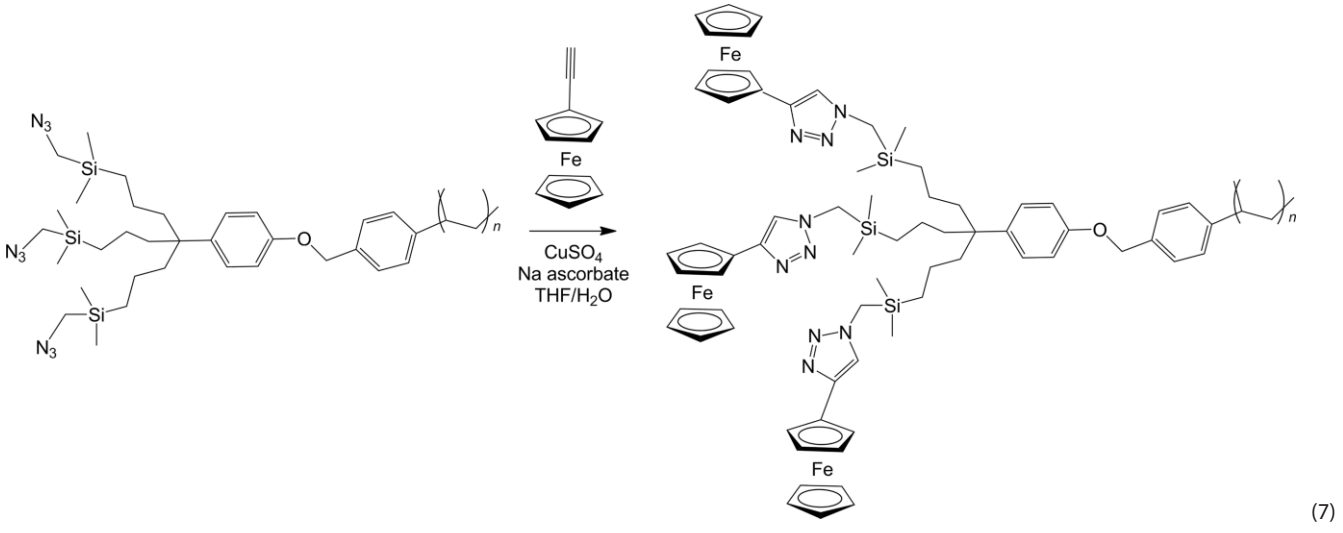
[Equation (6)] and of small oligomers with two to seven monomer units proved remarkable, with the observations being found to depend on whether the oligomer contained an odd or an even number of ferrocene units. For oligomer systems containing odd numbers of ferrocene units two reversible redox CV waves were observed, with a redox splitting of 0.22 V, whereas for oligomer systems containing even numbers of ferrocene units larger than two, three CV waves of varying intensities were observed. For large polymers there were two reversible CV redox processes of equal intensity at 0.00 and 0.24 V versus FcH. As shown in Equation (6), the successive ferrocenyl groups are very close to one another, so that oxidation of two successive groups at once cannot occur because of the significant additional coulombic (electrostatic) repulsion between two neighboring groups. This is negligible, however, when oxidation proceeds at alternative groups. Thus, initial oxidation proceeds at alternative iron sites to afford mixed-valent dinuclear fragments. Further oxidation of successive groups occurs at a slightly higher potential. This explains the presence of two oxidation waves in the cases of the polymers and of small oligomers with odd numbers of units.[176] This metallopolymer field has provided a large variety of materials, some with potential applications, until very recently. For instance, the polyferrocenylsilanes can themselves be functionalized.[177] Nanostructured materials based on these polyferrocenylsilanes with emerging applications were found in the form of functional block copolymers.[178]

The syntheses of metallopolymers containing ferrocene units in the side chains proceed either through polymerization of monofunctional ferrocene derivatives containing a polymerizable substituent such as, typically, vinylferrocene under radical, cationic, anionic, or Ziegler–Natta conditions or by post-synthetic functionalization of a polymer. For this latter type, click chemistry is especially appropriate, because relevant reactions are easy to conduct under mild conditions. Thus for instance, poly(*p*-azidomethyl)-substituted derivatives were condensed with ethynylferrocene in a $Cu^{I}$-catalyzed alkyne–azide cycloaddition (CuAAC) process to yield 1,2,3-triazolylferrocene-containing dendronized polymers [Equation (7)].[179]

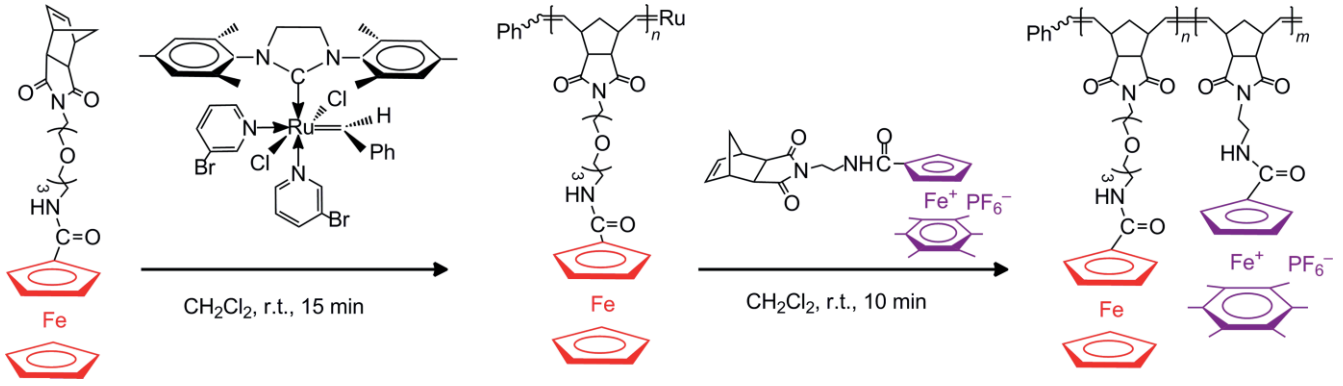
Other remarkable ferrocene-containing polymers are Nishihara's photoconducting poly-(1,1′-dihexylferrocenylenes)/TCNE adduct, astutely synthesized by the reaction between dihexylfulvalene dianion and $[FeCl_2(THF)_2]$, followed by charge transfer with TCNE,[180] and the borylene-bridged poly(ferrocenylene)s synthesized by Wagner's group.[181]

Ferrocenyl glycidyl ether and allyl glycidyl ether were recently copolymerized by living anionic ROP by the groups of Wagner, Frey, and Wurm to generate polyfunctional copolymers with molecular weights up to 40300 g $mol^{-1}$ and low molecular weight dispersities ($Mw/Mn < 1.18$).[182]

Radical addition fragmentation chain transfer (RAFT) polymerization and atom transfer radical polymerization (ATRP) of ferrocene-containing acrylate monomers have also recently become popular methods for the formation of polymers containing ferrocene units in their side chains. ROMP in the presence of the Schrock molybdenum high-oxidation-state alkylidene catalyst produced the first ferrocene-containing polymers by this method. Subsequently, a number of other ferrocene-containing polymers were synthesized by ROMP in the presence of the Schrock molybdenum–alkylidene or the Grubbs ruthenium–alkylidene catalysts.[183–187] Very recently, the synthesis of such ferrocene-containing polymers has been largely developed




(7)




Scheme 11. Living synthesis of diblock polymers containing ferrocene and iron sandwich units with the aid of the third-generation Grubbs ruthenium–benzylidene ROMP catalyst.[197]

with the aid of the third-generation Grubbs catalyst, because the catalyst is both very efficient and air-stable.[188,189] It reliably provides living polymers in a process that allows the introduction of several blocks containing solubilizing polyethyleneglycol (PEG) groups and additional neutral or cationic transition-metal sandwich complexes for multiple functions and applications (Scheme 11).[190–204]

Metallopolymers containing ferrocene units have been applied for redox-triggered release of a dye from patchy nanocapsules,[205] for switching of surface wettability,[206] in memory devices, and for permselective membrane gating.[207–212] A good number of reported polymers are water-soluble as a result of the introduction of PEG or polyelectrolyte blocks.[169,171,173,213,214]

## Ferrocene Polymers for Cathodic Battery Materials

Polymers with ferrocene-containing side chains show useful properties including air stability, fast electrochemical kinetics, and stable voltage plateaux for the development of cathodic battery materials.[215–220] Such polymers are electrically insulating, however, which limits their use as energy storage materials to small thicknesses, because fast charging/discharging kinetics are required. The electronic conductivity can be enhanced, however, by introduction of conductive polymers. Goodenough et al. reported a ferrocene-containing polypyrrole cathodic material with 65 mA h $g^{-1}$ at 0.2 C and up to 2 μm thickness,[215] whereas Su et al. reported ferrocene–pyrrole-, ferrocene–triphenylamine-, and ferrocene–aniline-based polymers reaching 68–104 mA h $g^{-1}$.[216] Ferrocene polymers have also been used as battery materials after carbon fillers were loaded into the polymer matrixes.[217–220] Walder's group recently reported a way to disperse negatively charged graphene oxide (GO) single sheets with partially oxidized poly(vinylferrocene) through electrostatic interactions with use of polymer/GO weight ratios of up to 10:1. Remarkably, these authors found that a film of (PVFc@rGO)@CC (current collector) with a specific capacity of 5.8 mC $cm^{-2}$ was >98 % charged/discharged in less than 3 s, and that increasing the layer thickness up to ca. 29 μm yielded a capacity of 770 mC $cm^{-2}$ accompanied by just 1 % capacity fade.[220]

## Ferrocenes in Supramolecular Ensembles, Liquid Crystals, and Nonlinear Optical Materials

Ferrocene units have also been included in macrocycles such as cryptands, calixarenes, and other endoreceptors, in particular by Beer's group for application in anion redox sensing. A large number of such ferrocene-containing endoreceptors have been synthesized and applied to anion sensing by this group,[221] and the area has been the subject of excellent reviews (Figure 2).[221,222]

More recently, activity along these lines has been pursued with ion-pair recognition and sensing in aqueous solution.[223] Ferrocene-appended interlocked structures such as rotaxanes were shown by Beer and co-workers by $^1$H NMR spectroscopy and electrochemistry to be selective for the recognition of chloride over more basic oxoanions, in marked contrast to acyclic analogues.[224–228] The same group designed a 1,2,3,4,5-pentaphenylferrocene-stoppered rotaxane that could electrochemically recognize anions.[229] A ferrocene-containing bis(triazolium)-based macrocyclic system was also shown to recognize chloride and benzoate anions.[230] A ferrocene-based imidazophenanthroline dyad chemosensor designed by Tarraga's and Molina's group effectively recognized aqueous hydrogenpyrophosphate and the organic anions ADP and ATP through three different channels, provoking cathodic shifts of the ferrocene CV wave ranging from –130 mV for hydrogenpyrophosphate and fluoride to –40 mV for ADP.[231] Ferrocene-based ureas have also been used as receptors of $H_2PO_4^-$ and fluoride anions.[232]

The ferrocene unit can be not only part of the host, but also part of a guest in supramolecular ensembles. For instance, Kaifer's group reported binding interactions between cucurbit[*n*]uril hosts (*n* = 7, 8) and guests such as 1,1′-bis(cyclohexylammoniomethyl)ferrocene, 1,1′-bis(cyclohexylmethylammoniomethyl)ferrocene, and 1,1′-bis(cyclohexyldimethylammoniomethyl)ferrocene in aqueous solution.[233–237]

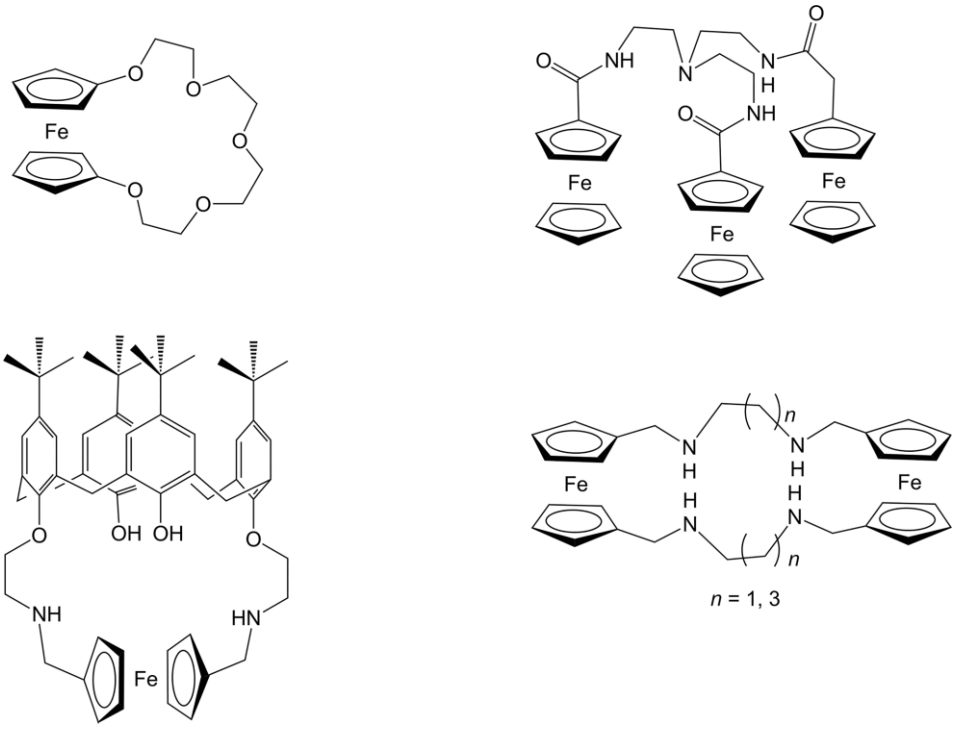



Figure 2. Examples of Beer's ferrocene-containing endoreceptors for anion redox recognition.[221] See Beer and Gale's general review.[356]

Ferrocenes such as the seminal example of *cis*-1-ferrocenyl-2-(4-nitrophenyl)ethylene (Figure 3, left) were found by Green's group,[238] followed by other groups,[239–248] to show nonlinear optical (NLO) properties, with applications in optical signal processing such as the frequency doubling of laser light.

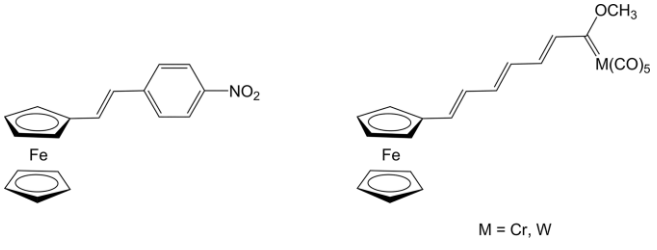
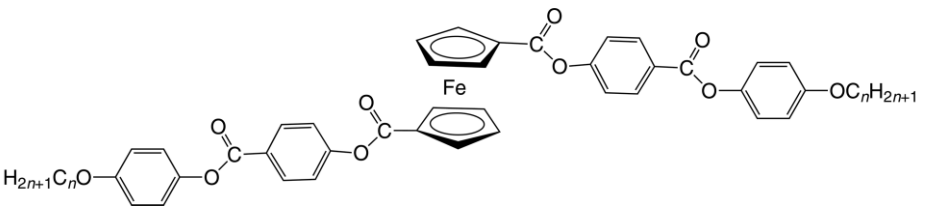



Figure 3. Green's (left)[238] and Nishihara–Sarkar's (right)[239] ferrocene-containing NLO active molecules.

The Nishihara–Sankar group designed a series of molecular ensembles in which ferrocene is conjugated with a Fischer carbene and disclosed NLO properties involving organometallic push-pull behavior. The molecular first hyperpolarizability ($\beta$) was determined by hyper-Rayleigh scattering experiments, and the $\beta$ values, ranging from $110 \times 10^{-30}$ to $2420 \times 10^{-30}$ esu in acetonitrile, are among the highest reported for organometallic molecules (Figure 3, right).[239] This field is presently very active, as is shown by selected recent examples. With a constant ferrocene donor and 4,4′-bipyridinium as the acceptor, variation of the conjugated bridges allowed the contributions of the organic connectors to chromophore NLO activities to be determined. It turned out that both the reduction reactions and the organic connectors had a significant influence on the 4,4′-bipyridinium system.[231] The groups of Hamon, Saillard, Carrillo, Manzur, and Ledoux-Rak developed another remarkable series of molecular systems in which ferrocene is conjugated with Schiff bases; excellent NLO properties were disclosed.[242–247] The largest quadratic hyperpolarizability value ($970 \times 10^{-30}$ esu) was determined for palladium-containing dimetallic ferrocene Schiff-base species.[246] Depending on their substitution patterns, these ferrocene Schiff-base complexes can be polymerized to form either main-chain oligomers[244] or side-chain metallopolymers,[247] showing a strong increase in the second-order NLO response.

Ferrocenes have often been employed in luminescent systems, because they quench excited states. Intra- or intermolecular quenching involve either energy or electron transfer. Other applications in luminescent materials with ferrocene as a redox sensor have been disclosed.[248,249]

Ferrocene-containing peptides are of great supramolecular (vide supra) and biomedical (vide infra) interest, as shown by the work of the groups of Kraatz, Metzler, and Rapic. For instance, these authors designed and studied helically chiral ferrocene peptides containing 1′-aminoferrocene-1-carboxylic acid subunits as turn inducers by means of, inter alia, the very useful circular dichroism technique. In particular, they showed that the helical chirality of the ferrocene system is governed solely by the chirality of the amino acid attached to the N-terminus of the ferrocenylamino acid. The conformation and hydrogen-bonding properties of ferrocenyl-labeled sugar amino acids were also examined by Barisic's and Rapic's groups. The Rapic and Zinic group established the formation of foldamers stabilized by the special type of aromatic π–π interactions between the closer cyclopentadienyl rings of the juxtaposed ferro-




cene units of bis- and tris(ferrocene)-containing *N*-methylimides.[250–255]

Ferrocenes have been incorporated in original thermotropic liquid crystals, in particular by the groups of Descheneaux[256–259] and Guillon[257,259] and more recently by Donnio's group.[259,260]

Deschenaux, Serrano, and Levelut designed and synthesized a ferrocene-containing liquid-crystalline first-generation dendritic core substituted with six mesomorphic ferrocene units and showed that these compounds exhibited a broad enantiotropic smectic A phase.[256] The groups of Guillon, Prato, and Deschenaux disclosed liquid-crystalline fullerene–ferrocene dyads and ferrocene-containing optically active liquid-crystalline side-chain polysiloxanes with planar chirality.[257]

Ferrocene has also been used in monolayers on gold[261] and silicon[262] surfaces, which could be applied to charge storage and communication devices. Ferrocene-appended porphyrins are potentially useful molecular materials in self-assembled monolayers for charge separation upon photoinduced electron transfer.[263]

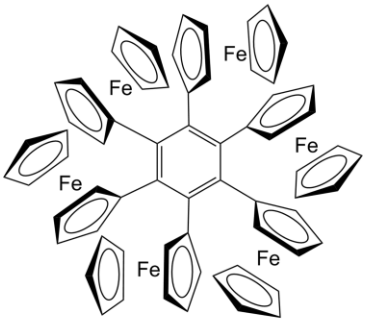
## Ferrocenes as Sources of Carbon Nanotubes and Other Materials

In the early days after the discovery of ferrocene, it was found that ferrocene and other ferrocenyl compounds could be used as antiknock agents and employed in the fuel for petrol engines for being safer than tetraethyllead. Iron from ferrocene is also used to cover spark plugs, improving electrical conductivity. Ferrocene-containing polymers have also been considered as aerospace materials.[264] Ferrocene has been used as a precursor material of iron NPs for the production of carbon nanotubes (CNTs) on heating a ferrocene/xylene mixture (other aromatics are also used) to 675 °C in a quartz-tube reactor.[265] Other ferrocene derivatives such as 1,1′-bis(diphenylphosphino)ferrocene have also been used for this purpose.[266–268] It was found that a good synthesis of carbon nanotubes used sublimed ferrocene that was decomposed under Ar, which allowed a good selection of the CNT diameter depending on the pressure and good yields for large-scale production.[269]

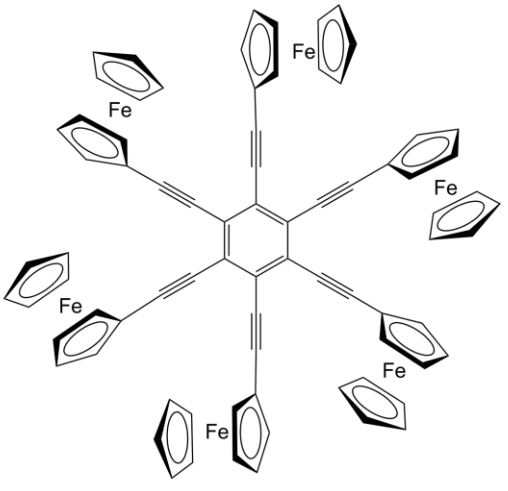
### Ferrocene-Containing Stars and Their Electrostatic Effects in Electron-Transfer Processes

The hexasubstituted benzene framework is ideal for the construction of hexaferrocene stars and the analysis of their remarkable redox, electrostatic, and electrochemical properties.[270] Stars terminated with ferrocene units include in particular highly crowded hexaferrocenylbenzene, synthesized by Vollhardt's group,[271] and hexakis(ferrocenylethynyl)benzene.[272,273]

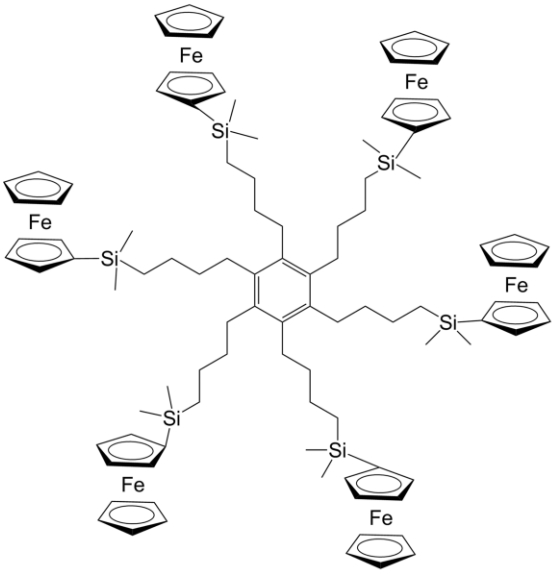
Because the ferrocene groups are located further from the central benzene core in hexakis(ferrocenyldimethylsilylbutyl)benzene and hexakis(pentamethylferrocenylethynylphenyl)benzene,[274] their electron-transfer and electrochemical properties become more independent from one another, and the ferrocene units are sufficiently remote from one another to present a single cyclic voltammetry (CV) wave with the standard electrolyte $n$Bu$_4$N$^+$PF$_6^-$.



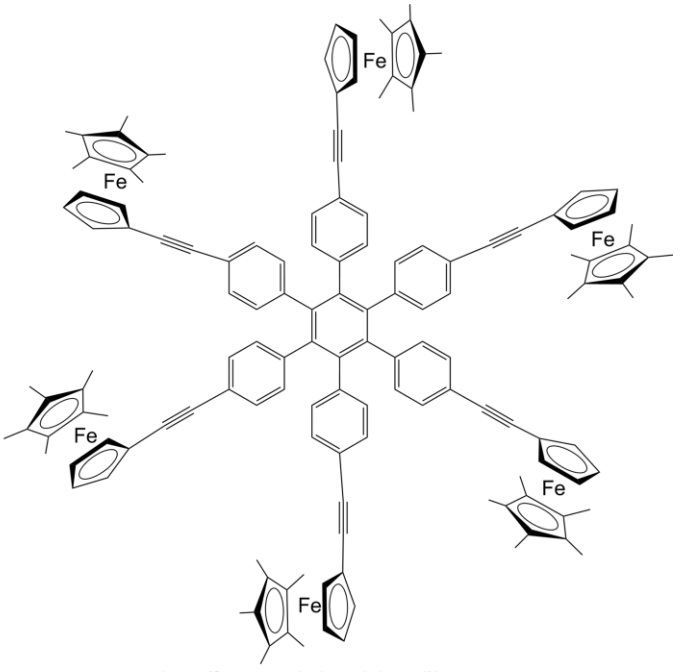

hexaferrocenylbenzene




hexa(ferrocenylethynyl)benzene




hexa(ferrocenyldimethylsilylbutyl)benzene




hexa(ferrocenylethynylphenyl)benzene

The ferrocenyl 6e CV wave seems to indicate that the six ferrocene units are equivalent and oxidized at the same potential, because the cyclic voltammogram appears analogous to that of a single electron wave. In fact, the six redox potentials will be theoretically slightly different because of the statistic factor even if the electrostatic factor is nil.[97] Moreover, this factor is not absolutely nil, although it is so minute that it is not observable (with the same molecular framework it is always more difficult to oxidize a monocation to a dication than a neutral molecule to a monocation due to coulombic repulsion; vide supra).[275] Conversely, as the ferrocene units become closer to the central benzene core and to one another, the electrostatic factor becomes more significant, and therefore multiple CV waves are observed. As shown by Geiger's group and others, close redox CV waves are better separated with use of electrolytes based on weakly coordinating anions such as tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate ($[BAr^F_4]^-$) and tetrakis-(pentafluorophenyl)borate $\{[B(C_6F_5)_4]^-\}$. These anions are more weakly bonded to ferricinium cations than other traditional anions such as $BF_4^-$ and $PF_6^-$ that are currently used as electrolyte anions. The ion-pairing strength of the more traditional anions with ferricinium cations or other cations shields their positive charge, thus lowering the $E_{1/2}$ values of multiply charged cations.[276–279] For instance, 1,3,5-tris(ferrocenylethynyl)benzene shows a single 3e CV wave with $n$Bu$_4$N$^+$PF$_6^-$[280,281] as the electrolyte, but three well-separated single-electron CV waves with $[BAr^F_4]^-$.[273] The lack of wave separation with $n$Bu$_4$N$^+$PF$_6^-$ shows a lack of electronic communication between the three ethynylferrocene groups in *meta* positions relative to one another, which indicates that the wave separation observed with $[n$Bu$_4$N$]^+[BAr^F_4]^-$ is purely electrostatic in origin (Figure 4).

Interestingly, in 1,4-bis(ferrocenylethynyl)benzene, only a single 2e CV wave is observed even with $[n$Bu$_4$N$]^+[BAr^F_4]^-$ as electrolyte, showing the absence of any significant electrostatic effect when these two ferrocenylethynyl substituents are in a *para* relationship. This is due to the fact that the rotation of the Fc groups allows them to be in a transoid relationship with respect to each other, which involves the maximum distance between the two iron redox centers. For hexakis(ferrocenylethynyl)benzene, three distinct 2e CV waves are also observed with $[n$Bu$_4$N$]^+[BAr^F_4]^-$ (Scheme 12) but only a single 6e wave with $n$Bu$_4$N$^+$PF$_6^-$, which corroborates the above finding observed with 1,4-bis(ferrocenylethynyl)benzene and with 1,3,5-tris(ferrocenylethynyl)benzene: that is, *para* substituents are independent, but not those in *ortho* and *meta* relationships. This striking difference in electrostatic effect between the *meta* and

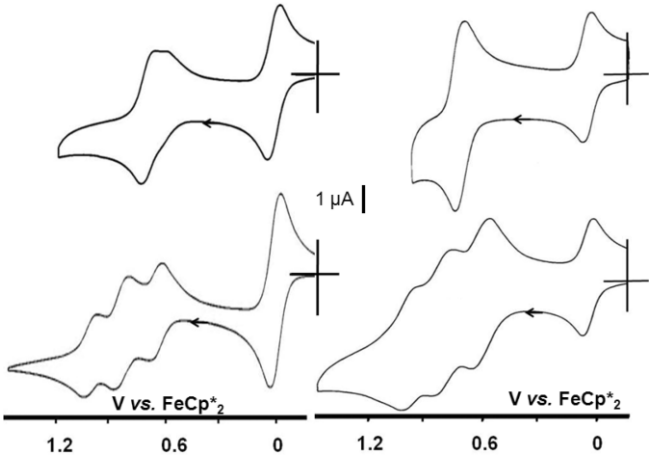
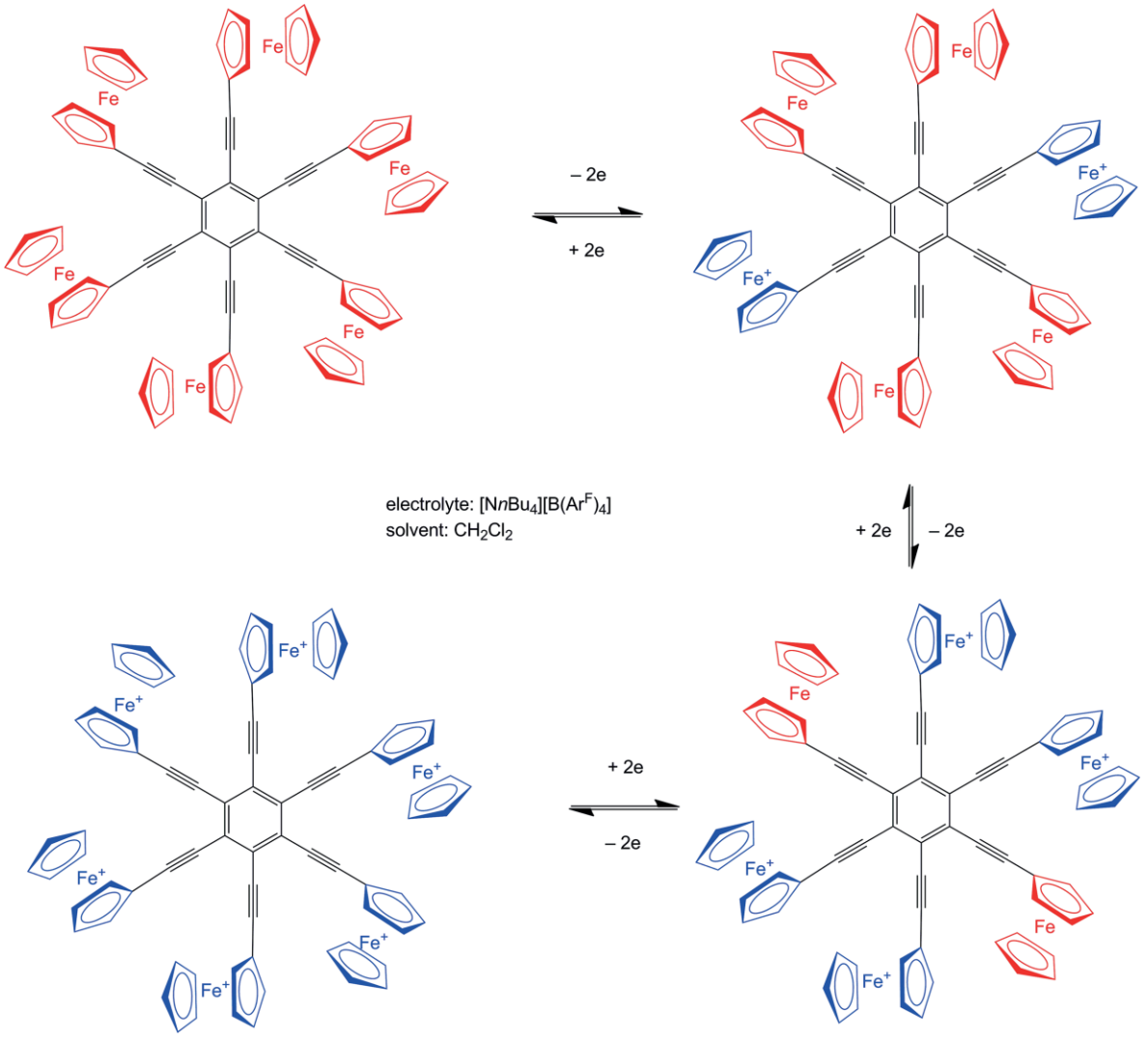



Figure 4. Comparison of cyclic voltammograms of 1,3,5-tris(ferrocenylethynyl)benzene (left) and hexakis(ferrocenylethynyl)benzene (right; see Scheme 1) in $CH_2Cl_2$ with $[(n\text{Bu})_4\text{N}][PF_6]$ (top) and $[(n\text{Bu})_4\text{N}][BAr^F_4]$ {bottom; $Ar^F = 3,5\text{-}C_6H_3(CF_3)_2$}.




Scheme 12. Anodic oxidation of hexakis(ferrocenylethynyl)benzene with $NBu_4BAr^F_4$ as electrolyte in $CH_2Cl_2$: electrostatic effects are observed between a ferrocene center and those in *ortho* and *meta* (but not in *para*) positions, resulting in three 2e CV waves (see Figure 4).[272,273]

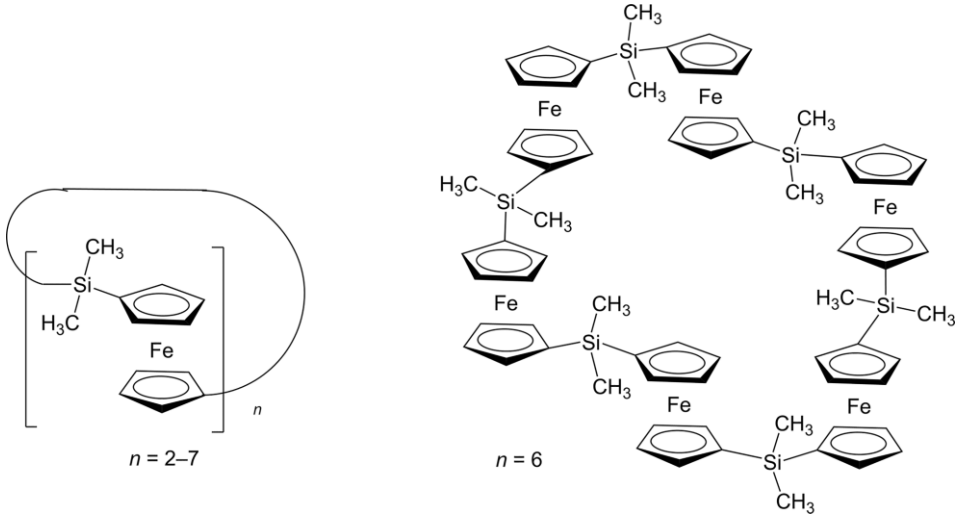



Figure 5. Manners' sexi-ferrocenylsilyl cyclic oligomer. The electrostatic effect is observed between a ferrocene center and its first neighbor, but not with the second and third neighbors, resulting in the presence of two 3e CV waves.[283]

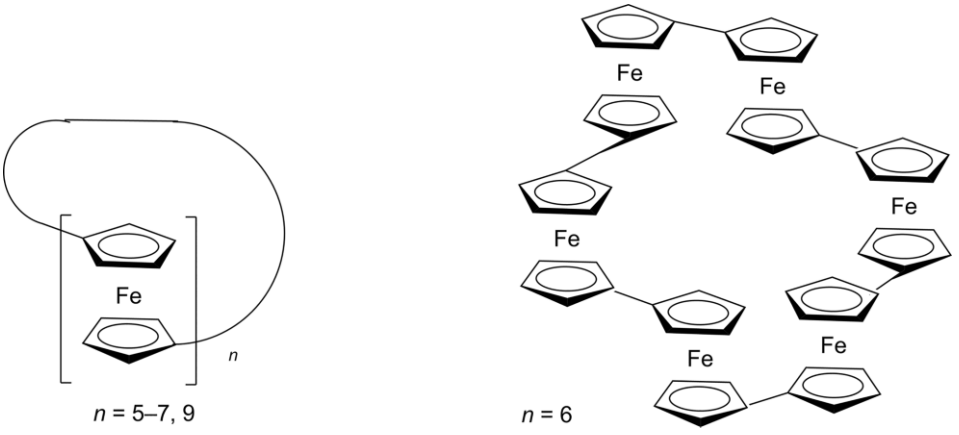



Figure 6. Long's sexi-ferrocene cyclic oligomer. The electrostatic effect is observed between a ferrocene center and first, second, and third neighbors, resulting in four individual 1e waves within the CV window (the two others lying outside).[284]

*para* positions was explained in terms of the substituents in 1,3,5-positions not being able to move apart from one another.[273]

Interestingly, a number of cyclic oligoferrocenes containing more than two ferrocene units are known;[249,282–284] in particular, a cyclic doubly bridged heptaferrocene reported by Köhler,[282] cyclic oligoferrocenes containing from two to seven ferrocenyldimethylsilyl groups by Manners' group,[283] and, most recently, oligomeric ferrocene rings with five to seven and with nine ferrocene moieties by Albrecht's and Long's groups.[284] For the cyclic ferrocenylsilane oligomers, well-separated 1e waves were only observed with up to three $FcSiMe_2$ units. For instance, for the hexa(ferrocenylsilane) ring (Figure 5), two 3e waves separated by 0.2 V were observed, due to the weak electrostatic factor and the absence of any significant intramolecular electronic factor.

For the series of oligomeric ferrocenes with five to seven and with nine ferrocene moieties (Figure 6), the ferrocenyl groups are directly bonded to one another. Thus, the mixed electronic and electrostatic effects are larger, and individual 1e CV waves reflect class-II mixed valency as in biferrocene (vide supra). The numbers of 1e CV waves observed in the electrochemical window (only three for cyclo[5], four for cyclo[6], and six for cyclo[9]) are lower than the numbers of ferrocene units in the rings, due to the increasingly large coulombic effect as the number of oxidized ferrocene units increases within a given ring.[284]

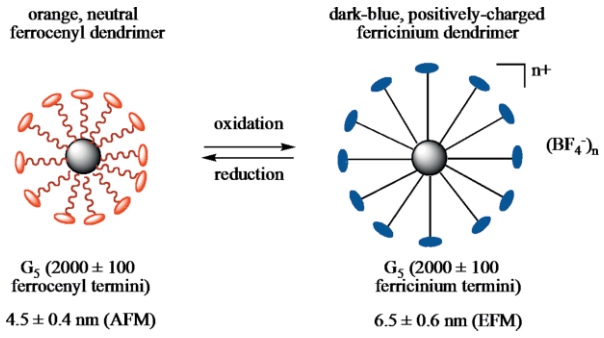
## Ferrocene-Containing Dendrons, Dendrimers, and NPs and Their Application in Redox Sensing and Catalysis

Since the seminal reports in the 1990s,[285–289] there have been a considerable number of reports on the syntheses of ferrocene dendrimers.[290–294] In 1997, the first amidoferrocene dendrimers were reported to be excellent sensors in the redox recognition of oxoanions.[288] A required condition for the usage of a metallodendrimer as a redox sensor is the equivalence of all the peripheral redox groups (i.e., the absence of significant electrostatic effects noted in the previous section), so that the CV wave of the ferrocene dendrimer will be unique and chemically and electrochemically reversible. Upon addition of the $nBu_4N^+$ salt of the oxoanion $HSO_4^-$ or $H_2PO_4^-$ to the solution of the metallodendrimer, a new ferrocenyl CV wave appears, resulting from the H-bonding interactions between the anion and the amidoferrocene group. The shift of the new CV wave with respect to the initial ferrocenyl CV wave is all the larger if the dendrimer is of higher generation, which can be explained in terms of the creation of narrower channels between the terminal tethers for tighter amidoferrocene–oxoanion interactions.[288,294]

The construction of gold NPs (AuNPs) containing thiolate ligands terminated with ferrocene[295,296] or biferrocene[63–65,297–299] ligands or dendrons[296] offers molecular assemblies with multiple equivalent ferrocene or biferrocene groups. With dimethylsilylferrocene termini, the interaction between oxophilic silicon-based groups and oxoanions also produces appreciable perturbation of the ferrocene redox wave, inducing the appearance of a new wave that allows oxoanion titration. With such large molecular ensembles, full adsorption onto the Pt anode occurs upon multiple scanning of the potential around the ferrocene region, easily forming a dendrimer-derivatized electrode that can be washed after titration without removing the dendritic coating and reused multiple times.[296]

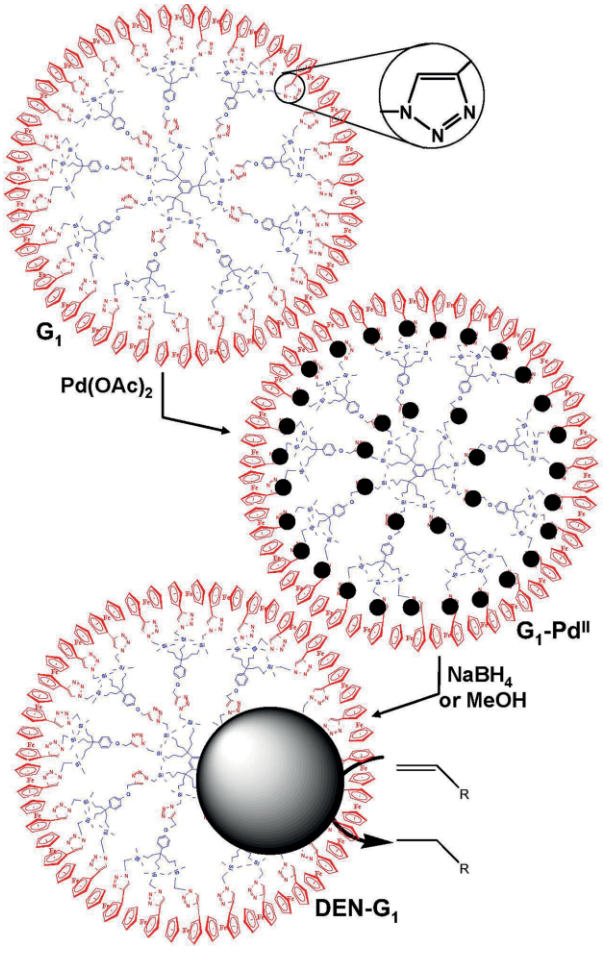
The first syntheses of clicked 1,2,3-triazolylferrocene-terminated dendrimers in 2007[300] and of clicked 1,2,3-triazolylbiferrocene-terminated dendrimers of several generations in 2010[301] offered the potential for redox sensing of oxoanions and transition-metal cations at the same time, again with positive dendritic effects (i.e., increased ion–dendrimer interactions as the dendrimer generation increased). Indeed, interaction of the intradendritic triazole groups with the transition-metal cations $Cu^I$, $Cu^{II}$, $Pd^{II}$, and $Au^{III}$ led to their redox recognition by cyclic voltammetry.[301,302] Various other ferrocene-containing dendrimers have been reported, their electrochemical properties providing useful information on interfacial electron-transfer properties and redox-recognition features.[303–308] Giant ferrocene-terminated dendrimers containing up to 15000 ferrocene or pentamethylferrocene termini were synthesized, and both the ferrocene and ferricinium forms were characterized by electronic microscopy with the termini showing the redox "breath-

ing" like molecular machines between the reduced and oxidized forms, the latter experiencing coulombic repulsion between charges that expanded the polycationic metallodendrimer size [Equation (8)].[305]

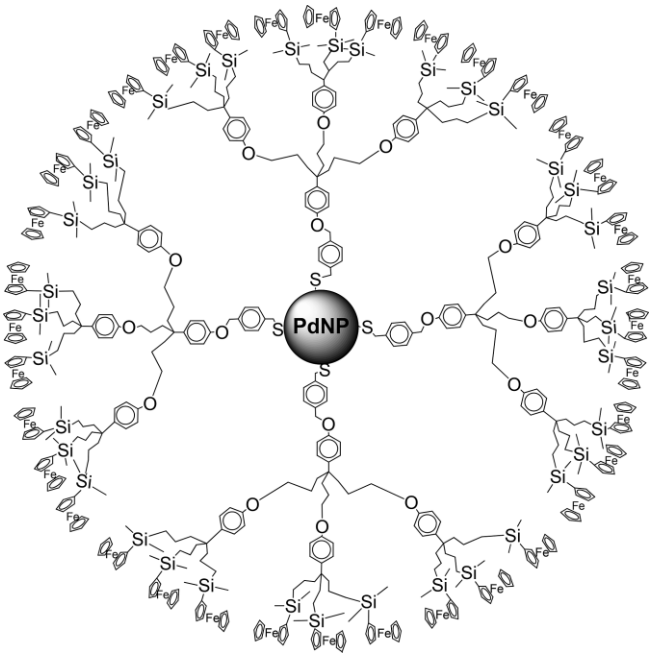



(8)

Click ferrocenyl dendrimers of zeroth (G0), first (G1), and second generation (G2), containing 9, 27, and 81 triazolylferrocenyl termini, respectively, were shown to stabilize highly catalytically active PdNPs through the intradendritic triazole ligands.[309] With G0, the PdNPs were too large to be encapsulated, but they were stabilized by several dendrimers. With G1 and G2, the PdNPs were encapsulated in the click dendrimers, the PdNP




Scheme 13. One-to-one complexation of intradendritic triazole ligands by $Pd^{II}$ followed by reduction to catalytically active $Pd^0$ NPs.[309]




core size fitting well with the theoretical size calculated from the number of Pd atoms corresponding (by transmission electron microscopy) to the interaction of one $Pd^{II}$ atom per intradendritic triazole ligand (Scheme 13).

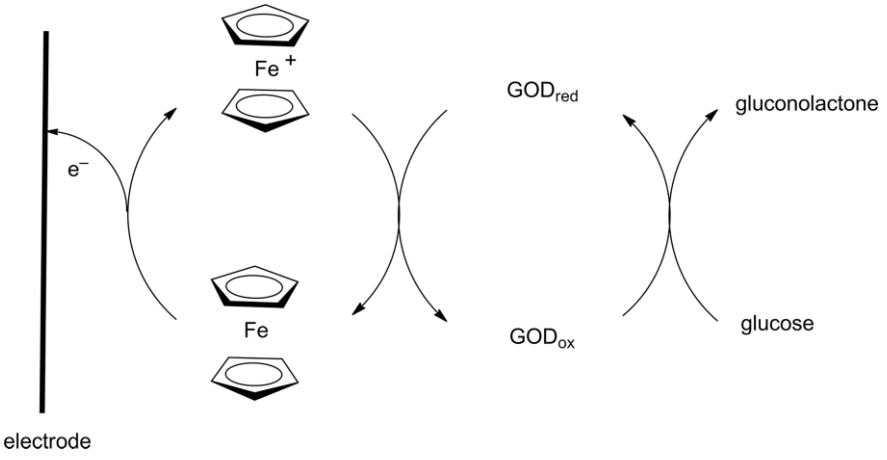
The yields of Suzuki–Miyaura cross-coupling reactions under ambient conditions were improved upon decreasing the catalyst concentration down to the ppm level, and were independent of the generation number and the type of stabilization (intra- or interdendritic).[309] A remarkable TON of 540000 was obtained at a concentration of 1 ppm of Pd. Thus, this "homeopathic"-type behavior,[310,311] together with these features, suggested that a leaching mechanism was occurring, similarly to what had been noted by de Vries for high-temperature Heck reactions.[312]

PdNP-cored ferrocenyl dendrimers also showed excellent catalytic activity at the PdNP core for Suzuki–Miyaura reactions; the ferrocene termini served as bulky fragments to stabilize small active PdNPs and also as nanofilters for styrene hydrogenation.[313]

## Ferrocenes in Nanomedicine

Organometallics are of considerable interest in medicine,[314–322] with the ferrocene/ferricinium redox couple being especially intensively studied. It is currently used as a redox mediator for the amperometric detection of glucose in blood, important for blood analysis of diabetic patients. Ferricinium formed at the anode oxidizes the reduced form of glucose oxidase enzyme ($GOD_{red}$), and the oxidized form of the enzyme ($GOD_{ox}$) then oxidizes the glucose substrate to gluconolactone. This organoiron redox couple rapidly shuttles electrons from GOD to electrodes (Scheme 14).

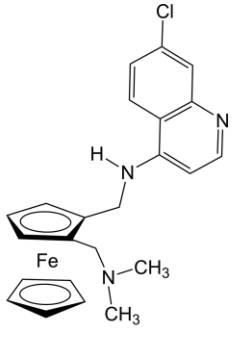
Consequently, the current that flows through the electrode is a measure of the glucose concentration.[323,324] The first pen-



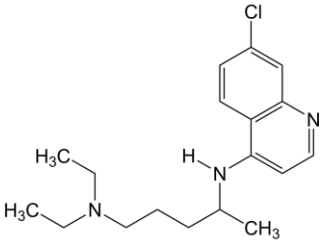

Scheme 14. GOD- and ferrocene-mediated anodic oxidation of glucose to gluconolactone used as a universal amperometric sensor for the convenient and fast detection of glucose in blood.[322]

sized electrochemical blood-glucose monitor for self-monitoring for diabetic people was disclosed by Higgins, Hill, and Plotkin and launched in 1987 as the ExacTech blood glucose meter by Genetics International Inc. of Cambridge, MA; $10^{10}$ glucose assays annually are performed by self-monitoring with this method.[325]

The most used ferrocene-based drug in medicine is the antimalarial drug ferroquine, established by Biot's group in Lille and presently in clinical phase IIb.[326] This compound incorporates ferrocene in the basic structure of chloroquine, the most commonly used antimalarial drug. Chloroquine suffers from a heavy resistance problem that appears to be avoided with the presence of the ferroquine moiety, due to production of free radicals through organoiron redox activity. This organoiron drug has also recently been found to inhibit infection by the hepatitis C virus.[327]




Ferroquine, anti-malarial drug, avoids the resitance to chloroquine




Chloroquine, first synthetic anti-malarial drug

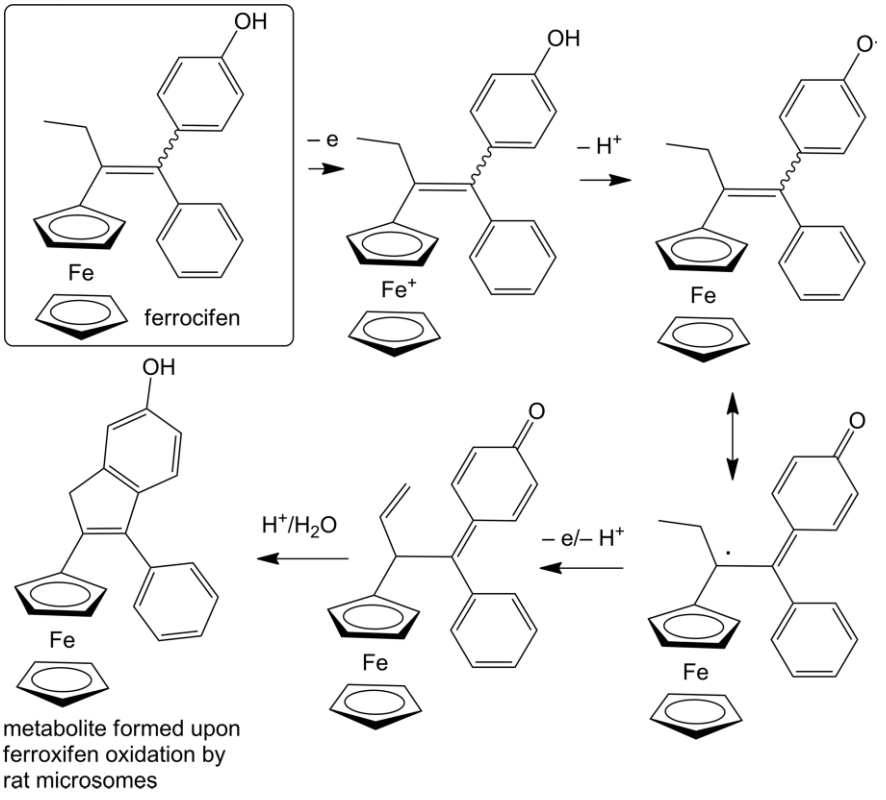
Antitumor activities of ferrocenes were first reported in 1978 by Brynes' group, with derivatives bearing an amine or amido group that were active against lymphocytic leukemia P-388.[328] Subsequently, several types of ferrocene derivatives were studied for their anticancer activity and have been excellently reviewed and classified by Ornelas.[315] These types of anticancer results with ferrocenes are as follows:

(i) Ferricinium salts were first shown, by Köpf-Maier, Köpf, and Neuse in 1984, to be efficient against tumor-bearing Ehrich ascites with counter-anion-dependent activity[329] as a consequence of Fenton-type oxygen radicals [reactive oxygen species (ROSs)] causing DNA damage and apoptosis of cells.[330] In 1989 Neuse's group reported ferricinium-containing water-soluble polymers that exhibited cytotoxicity, although the instability of the ferricinium group limited potential applications. Further studies by this group involved the solubilization of ferrocene-containing polymers through the introduction of polyaspartamide modified with PEG side chains and antiproliferative activity against HeLa and NCaP human cancer cell lines (IC values: 2–20 mg of Fe $\mu L^{-1}$).[331]

(ii) Ferrocene units conjugated to biologically active molecules including ferrocenylalkylazoles, ferrocene conjugated with peptides, ferrocenylalkyl nucleobases, ferrocenyl derivatives of illudin M, and ferrocenyl derivatives of retinoids.[332,333]

(iii) DNA-targeting compounds connected to ferrocene, including ferrocene connected to a DNA intercalator and ferrocene derivatives of inhibitors of topoisomerase II.[334]

(iv) Ferrocenyl compounds based on selective estrogen modulators, including ferrocifens, ferrociphenols, and ferrocenophanes, studied in depth by the Jaouen–Veissière–Top–Hillard group (in these compounds a phenyl ring of the currently widely used drug tamoxifen or a derivative is replaced by a ferrocenyl unit[335–339]), as well as ferrocenylraloxifen, studied by the Marques group.[340] These compounds show promising results for breast cancer. In particular, the antiproliferative effect of ferrocifens is linked to the formation of ROSs (as in the seminal examples reported by Köpf-Maier, Köpf, and Neuse with simple ferricinium salts), which has been shown by the loss of these effects upon addition of antioxidants. This ROS formation is not linked to the phenol group, however, because the first oxidation step of ferrocifens is ferrocene oxidation to ferricinium. Note that the $IC_{50}$ values of the initial simple ferricinium complexes are much larger than those of the ferrocifens (250 μM vs. 0.5 μM). In the presence of a base such as pyridine, the hydroxyferrocifens are oxidized to quinonemethides through a double coupled electron–proton transfer, and these quinonemethides have been identified as metabolites formed upon oxidation of ferrocifens by rat microsomes (Scheme 15). The formation of




Scheme 15. Mechanism of the oxidation of ferrocifen by rat microsomes.[339]

quinonemethides does not appear necessary for the observation of strong antiproliferative effects, however.[339]

(v) Ferrocenylandrogens and -antiandrogens, including ferrocene derivatives of testosterone and dihydrotestosterone and ferrocene derivatives of nilutamide.[341]

(vi) Ferrocene-derived ligands coordinated to transition-metal ions including those of Ru, Rh, Ir, Pd, Pt, and Au.[342,343]

Most recently, ferrocene-related anticancer research is also focusing on ferrocene–chalcogeno-triazole–sugar conjugates,[344] membrane interactions of nitroarylferrocenes,[345] PEGylated ferrocene radiosensitizers of cancer cells,[346] tubulin-binding ferrocene-substituted 3,3′-diindolylmethane,[347] ferrocene-modified phospholipids,[348] ferrocene–iminosugar hybrids,[349] ferrocene–N-heterocyclic carbene–gold(I) complexes targeting antioxidant pathways,[350] and dendrimer-related strategies.[351] In terms of drug delivery, an elegant approach was reported by Wang's group with pH-responsive supramolecular vesicles based on water-soluble pillar[6]arene and ferrocene derivatives.[352]

## Conclusion and Outlook

Why is ferrocene so exceptional? From its origins in modern hard-core organometallic chemistry it has now reached a place of prominence in the toolbox of molecular chemistry and materials science. This situation is due to its low price, robustness, and easy handling, even for first-year students, and mainly the extraordinary richness of its steroelectronic properties that have provided hundreds of catalysts including many efficient chiral ones and molecular material precursors for a variety of applications. Of crucial interest is the coupling of its versatile redox properties with key applications in fields such as nanomedicine, biological sensing, catalysis, battery and other materials, and other areas involving supramolecular, macromolecular, and optoelectronic property aspects. Thanks to the diversity of its properties and functions and the richness and ease of its functionalization possibilities, ferrocene is set to be the subject of increased research density directed towards molecular materials, with a bright future in nanosciences.

## Acknowledgments

Invaluable contributions from and discussions with past and present group members cited in the references and financial support from the University of Bordeaux, the Centre National de la Recherche Scientifique (CNRS), the Institut Uiversitaire de France (IUF), the Ministère de l'Enseignement Supérieur et de la Recherche (MESR), the Chinese Research Council (CRC), and l'Oréal are gratefully acknowledged.

**Keywords:** Ferrocene · Metallocenes · Electron transfer · Organometallic chemistry · Molecular engineering · Nanostructures · Redox chemistry

[1] I. Langmuir, *Science* **1921**, *54*, 59–67.
[2] N. V. Sidgwick, *Trans. Faraday Soc.* **1923**, *19*, 469–475.
[3] T. J. Kealy, P. L. Pauson, *Nature* **1951**, *168*, 1039–1040.
[4] S. A. Miller, J. A. Tebboth, J. F. Tremaine, *J. Chem. Soc.* **1952**, 632–635.

[5] G. Wilkinson, M. Rosenblum, M. C. Whiting, R. B. Woodward, *J. Am. Chem. Soc.* **1952**, *74*, 2125–2126.
[6] E. O. Fischer, W. Pfab, *Z. Naturforsch. B* **1952**, *7*, 377–379.
[7] R. B. Woodward, M. Rosenblum, M. C. Whiting, *J. Am. Chem. Soc.* **1952**, *74*, 3458–3459.
[8] M. Rosenblum. *Chemistry of the Iron Group Metallocenes, Part I*, Interscience, New York, **1965**.
[9] *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science* (Eds.: A. Togni, T. Hayashi), Wiley-VCH, Weinheim, **1995**.
[10] *Ferrocenes: Ligands, Materials and Biomolecules* (Ed.: P. Stepnicka), Wiley, **2008**.
[11] *Ferrocenes: Compounds, Properties and Applications* (Ed.: E. S. Phillips), Nova Science Publishers, **2011**.
[12] G. Wilkinson, *J. Organomet. Chem.* **1975**, *100*, 273–278.
[13] T. M. Zydowsky, *Chem. Intell.* **2000**, 29–34.
[14] P. Laszlo, R. Hoffmann, *Angew. Chem. Int. Ed.* **2000**, *39*, 123–124; *Angew. Chem.* **2000**, *112*, 127.
[15] P. L. Pauson, *J. Organomet. Chem.* **2001**, *637–639*, 3–6.
[16] E. O. Fischer, R. Jira, *J. Organomet. Chem.* **2001**, *637*, 7–12.
[17] R. Dagani, *Chem. Eng. News* **2001**, *79*, 37–38.
[18] H. Werner, *Angew. Chem. Int. Ed.* **2012**, *51*, 6052–6058; *Angew. Chem.* **2012**, *124*, 6156–6152.
[19] J. L. Robbins, N. M. Edelstein, S. R. Cooper, J. C. Smart, *J. Am. Chem. Soc.* **1979**, *101*, 3853–3857.
[20] G. Wilkinson, *J. Am. Chem. Soc.* **1952**, *74*, 6148–6149.
[21] W. E. Geiger, *Organometallics* **2007**, *26*, 5738–5785.
[22] D. W. Macomber, W. P. Hart, M. D. Rausch, *Adv. Organomet. Chem.* **1982**, *21*, 1–55.
[23] M. Rosenblum, R. B. Woodward, *J. Am. Chem. Soc.* **1958**, *80*, 5443–5444.
[24] R. E. Bozak, *J. Chem. Educ.* **1966**, *43*, 73–73.
[25] C. J. Donahue, E. R. Donahue, *J. Chem. Educ.* **2013**, *90*, 1688–1691.
[26] M. Cais, A. Eisenstadt, *J. Org. Chem.* **1965**, *30*, 1148–1154.
[27] A. Horeau, H. B. Kagan, *Tetrahedron* **1964**, *20*, 2431–2441.
[28] D. E. Hamilton, *J. Chem. Educ.* **1991**, *68*, A143–A144.
[29] S.-Y. Xu, B. Hu, S. E. Flower, Y. B. Jiang, J. S. Fossey, W. P. Deng, T. D. James, *Chem. Commun.* **2013**, *49*, 8314–8316.
[30] Y. Wang, T. Lin, R. Shyu, J. Hwu, Y. Wang, M. Cheng, *J. Organomet. Chem.* **1989**, *371*, 57–69.
[31] T. Mikhailova, N. Marshall, *ChemSpider* **2014**, DOI: 10.1039/SP759; http://cssp.chemspider.com/article.aspx?id = 759.
[32] R. Shi, H. Wang, P. Tang, Y. Bin, *Front. Chem. Sci. Eng.* **2014**, *8*, 171–178.
[33] A. N. Nesmeyanov, V. A. Savanova, V. N. Drovn, N. A. Radinov, *Dokl. Akad. Nauk SSSR* **1965**, *160*, 355–356.
[34] R. M. Gleixner, K. M. Joly, M. Tremayne, B. M. Kariuki, L. Male, D. M. Coe, L. R. Cox, *Chem. Eur. J.* **2010**, *16*, 5769–5777.
[35] J. Feinberg, M. Rosenblum, *J. Am. Chem. Soc.* **1969**, *91*, 4324–4325.
[36] P. Ashkenazi, S. Lupan, A. Schwarz, M. Cais, *Tetrahedron Lett.* **1969**, *10*, 817–820.
[37] A. DeHope, D. Mendoza-Espinosa, B. Donnadieu, G. Bertrand, *New J. Chem.* **2011**, *35*, 2037–2042.
[38] M. D. Rausch, D. J. Ciappene, *J. Organomet. Chem.* **1967**, *10*, 127–133.
[39] F. Rebière, O. Samuel, H. B. Kagan, *Tetrahedron Lett.* **1990**, *31*, 3121–3124.
[40] D. Guillaneux, H. B. Kagan, *J. Org. Chem.* **1995**, *60*, 2502–2505.
[41] D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann, I. Ugi, *J. Am. Chem. Soc.* **1970**, *92*, 5389–5990.
[42] F. Rebiere, O. Riant, L. Ricard, H. B. Kagan, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 568–570; *Angew. Chem.* **1993**, *105*, 644.
[43] A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994**, *116*, 4062–4066.
[44] A. Togni, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1475–1477; *Angew. Chem.* **1996**, *108*, 1581.
[45] O. Riant, O. Samuel, T. Flesner, S. Taudien, H. B. Kagan, *J. Org. Chem.* **1997**, *62*, 6733–6745.
[46] O. Riant, G. Argouarch, D. Guillaneux, O. Samuel, H. B. Kagan, *J. Org. Chem.* **1998**, *63*, 3511–3514.
[47] L. Schwink, P. Knochel, *Chem. Eur. J.* **1998**, *4*, 950–968.
[48] T. J. Colacot, *Chem. Rev.* **2003**, *103*, 3101–3118.
[49] P. Barbaro, C. Bianchini, G. Giambastani, S. L. Parisel, *Coord. Chem. Rev.* **2004**, *248*, 2131–2150.
[50] N. Debono, A. Labande, E. Manoury, J.-C. Daran, R. Poli, *Organometallics* **2010**, *29*, 1879–1882.
[51] M. M. Wei, M. Garcia-Melchor, J.-C. Daran, C. Audin, A. Lledos, R. Poli, E. Deydier, E. Manoury, *Organometallics* **2012**, *31*, 6669–6680.
[52] D. Schaarschmidt, H. Lang, *Organometallics* **2013**, *32*, 5668–5704 (review).
[53] E. A. Standley, S. Z. Tasker, K. L. Jensen, T. F. Jamison, *Acc. Chem. Res.* **2015**, *48*, 1503–1514.
[54] C. Gäbler, J. Speck, M. Korb, H. Lang, *J. Organomet. Chem.* **2016**, *813*, 26–35.
[55] Z. Y. Wu, P. Retailleau, V. Gandon, A. Voituriez, A. Marinetti, *Eur. J. Org. Chem.* **2016**, 70–75.
[56] T. Hayashi, M. Konishi, Y. Kobori, *J. Am. Chem. Soc.* **1984**, *106*, 158–163.
[57] O. Riant, O. Samuel, H. B. Kagan, *J. Am. Chem. Soc.* **1993**, *115*, 5835–5836.
[58] A. Togni, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1475–1477; *Angew. Chem.* **1996**, *108*, 1581.
[59] Z. Q. Weng, S. Teo, T. S. A. Hor, *Organometallics* **2006**, *25*, 4878–4882.
[60] W.-H. Zhang, S. W. Chien, T. S. A. Hor, *Coord. Chem. Rev.* **2011**, *255*, 1991–2024.
[61] C. Lopez, M. Salmi, A. Mas, P. Piotrowski, M. F. Bardia, *Eur. J. Inorg. Chem.* **2012**, 1702–1709.
[62] T. Horikoshi, M. Itoh, M. Kurihara, K. Kubo, H. Nishihara, *J. Electroanal. Chem.* **1999**, *473*, 113–116.
[63] M. Yamada, I. Quiros, J. Mizutani, K. Kubo, H. Nishihara, *Phys. Chem. Chem. Phys.* **2001**, *3*, 3377–3381.
[64] M. Yamada, H. Nishihara, *Langmuir* **2003**, *19*, 8050–8056.
[65] M. Yamada, T. Tadera, K. Kubo, H. Nishihara, *J. Phys. Chem. B* **2003**, *107*, 3703–3711.
[66] J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides, *Chem. Rev.* **2005**, *105*, 1103–1169.
[67] B. Bildstein, M. Malaun, H. Kopacka, K. Wurst, M. Mitterbock, K. H. Ongania, G. Opromolla, P. Zanello, *Organometallics* **1999**, *18*, 4325–4336.
[68] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877–910.
[69] R. Ciganda, J. Irigoyen, D. Gregurec, R. Hernández, S. Moya, C. Wang, J. Ruiz, D. Astruc, *Inorg. Chem.* **2016**, *55*, 6361–6363.
[70] M. Rosenblum, J. O. Santer, *J. Am. Chem. Soc.* **1959**, *81*, 5517–5518.
[71] N. Sharma, J. K. Ajay, K. Venkatasubbaiah, U. Lourderaj, *Phys. Chem. Chem. Phys.* **2015**, *17*, 22204–22209.
[72] I. Noviandri, K. N. Brown, D. S. Fleming, P. T. Gulyas, P. A. Lay, A. F. Masters, L. J. Philips, *J. Phys. Chem. B* **1999**, *103*, 6713–6722.
[73] J. Ruiz, M.-C. Daniel, D. Astruc, *Can. J. Chem.* **2006**, *84*, 288–299.
[74] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd edn. Wiley, New York, **2001**.
[75] W. E. Geiger in *Progress in Inorganic Chemistry* (Ed.: S. J. Lippard), Wiley, New York, **1985**, *33*, p. 275.
[76] H. Nishihara, *Adv. Inorg. Chem.* **2002**, *53*, 41–86.
[77] T. S. Zatsepin, S. Y. Andreev, T. Hianik, T. S. Oretskaya, *Russ. Chem. Rev.* **2003**, *72*, 537–554.
[78] Y. T. Long, C. Z. Li, T. C. Sutherland, H. B. Kraatz, *J. Am. Chem. Soc.* **2003**, *125*, 8724–8725.
[79] B. Adhikari, H. B. Kraatz, *Chem. Commun.* **2014**, *50*, 5551–5553.
[80] J. P. Hurvois, C. Moinet, *J. Organomet. Chem.* **2005**, *690*, 1829–1839.
[81] M. Kondo, M. Uchikawa, K. Namiki, W. W. Zhang, S. Kume, E. Nishibori, H. Suwa, S. Aoyagi, M. Sakata, M. Murata, Y. Kobayashi, H. Nishihara, *J. Am. Chem. Soc.* **2009**, *131*, 12112–12124.
[82] R. B. King, M. B. Bisnette, *J. Organomet. Chem.* **1967**, *8*, 287–297.
[83] J. S. Miller, J. C. Calabrese, R. L. Harlow, D. A. Dixon, J. H. Zhang, W. M. Reiff, S. Chittipeddi, M. A. Selover, A. J. Epstein, *J. Am. Chem. Soc.* **1990**, *112*, 5496–5506.
[84] S. Liu, K. Mase, C. Bougher, S. D. Hicks, M. M. Abu-Omar, S. Fukusumi, *Inorg. Chem.* **2014**, *53*, 7780–7788.
[85] J. Jung, S. Liu, K. Ohkubo, M. W. Abu-Omar, S. Fukusumi, *Inorg. Chem.* **2015**, *54*, 4285–4291.
[86] R. Deschenaux, M. Schweissguth, A. M. Levelut, *Chem. Commun.* **1996**, 1275–1276.
[87] M. Tropiano, N. L. Kilah, M. Morten, H. Rahman, J. J. Davis, P. D. Beer, S. Faulkner, *J. Am. Chem. Soc.* **2011**, *133*, 11847–11849.
[88] Y. Ochi, M. Suzuki, T. Imakoa, M. Murata, H. Nishihara, Y. Einaka, K. Yamamoto, *J. Am. Chem. Soc.* **2010**, *132*, 5061–5069.
[89] R. W. Murray, *Acc. Chem. Res.* **1980**, *13*, 135–141.
[90] A. Heller, *J. Phys. Chem.* **1992**, *96*, 3579–3587.
[91] H. Imahori, H. Norieda, H. Yamada, Y. Nishimura, I. Yamazaki, Y. Sakata, S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 100–110.

[92] C. J. Yu, Y. J. Wan, H. Yowanto, *J. Am. Chem. Soc.* **2001**, *123*, 1155–11161.
[93] T. G. Drummond, G. Hill, J. K. Barton, *Nat. Biotechnol.* **2003**, *21*, 1192–1199.
[94] A. Eckermann, D. L. Feld, J. A. Show, T. J. Maede, *Coord. Chem. Rev.* **2010**, *254*, 1769–1802.
[95] M. B. Robin, B. Melvin, P. Day, *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247–403.
[96] G. C. Allen, N. S. Hush, *Prog. Inorg. Chem.* **1967**, *8*, 357–390.
[97] D. E. Richardson, H. Taube, *Coord. Chem. Rev.* **1984**, *60*, 107–129.
[98] D. Astruc, *Electron Transfer and Radical Processes in Transition Metal Chemistry*, Wiley, New-York, **1995**, chapter 1.
[99] J.-P. Launay, *Coord. Chem. Rev.* **2013**, *257*, 1544–1554.
[100] M. Lacoste, F. Varret, L. Toupet, D. Astruc, *J. Am. Chem. Soc.* **1987**, *109*, 6504–6506.
[101] M. H. Desbois, D. Astruc, J. Guillin, F. Varret, *J. Am. Chem. Soc.* **1989**, *111*, 5800–5809.
[102] D. Astruc, *Acc. Chem. Res.* **1997**, *30*, 383–391.
[103] A. Hildebrandt, T. Rueffer, E. Erasmus, H. Lang, *Organometallics* **2010**, *29*, 4900–4905.
[104] A. Hildebrandt, D. Schaarschmidt, H. Lang, *Organometallics* **2011**, *30*, 556–563.
[105] A. Hildebrandt, H. Lang, *Organometallics* **2013**, *32*, 5640–5653.
[106] J. M. Speck, M. Kork, T. Ruffer, A. Hildebrandt, H. Lang, *Organometallics* **2014**, *33*, 4813–4823.
[107] U. Pfaff, A. Hildebrandt, M. Korb, H. Lang, *Polyhedron* **2015**, *86*, 2–9.
[108] K. Kowalski, R. Karpowicz, G. Mloston, D. Miesel, A. Hildebrandt, H. Lang, R. Czerwieniec, B. Therrien, *Dalton Trans.* **2015**, *44*, 6268–6276.
[109] D. Miesel, A. Hildebrand, H. M. Korb, D. A. Wild, P. J. Low, H. Lang, *Chem. Eur. J.* **2015**, *21*, 11545–11559.
[110] A. Ceccon, S. Santi, L. Orian, A. Bisello, *Coord. Chem. Rev.* **2004**, *248*, 683–724.
[111] M. Lohan, F. Justaud, H. Lang, C. Lapinte, *Organometallics* **2012**, *31*, 3565–3574.
[112] M. Kurosawa, T. Nankawa, T. Matsuda, K. Kubo, M. Kurihara, H. Nishihara, *Inorg. Chem.* **1999**, *38*, 5113–5123.
[113] M. Kurihara, T. Matsuda, A. Hirooka, T. Yutaka, H. Nishihara, *J. Am. Chem. Soc.* **2000**, *122*, 12903–12904.
[114] M. Murata, M. Yamada, T. Fujita, K. Kojima, M. Murihara, K. Kubo, Y. Kobayashi, H. Nishihara, *J. Am. Chem. Soc.* **2001**, *123*, 12903–12904.
[115] H. Nishihara, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 19–29.
[116] H. Nishihara, *Adv. Inorg. Chem.* **2002**, *53*, 41–86.
[117] A. Sakamoto, A. Hirooka, K. Namiki, M. Murihara, M. Murata, M. Sugimoto, H. Nishihara, *Inorg. Chem.* **2005**, *44*, 7547–7558.
[118] H. Nishihara, M. Murata, *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 147–156.
[119] R. Sakamoto, M. Murata, H. Nishihara, *Angew. Chem. Int. Ed.* **2006**, *45*, 4793–4795; *Angew. Chem.* **2006**, *118*, 4911.
[120] S. Muratsugu, S. Kume, H. Nishihara, *J. Am. Chem. Soc.* **2008**, *130*, 7204–7205.
[121] K. Kowalski, M. Linseis, R. F. Winter, M. Zabelk, S. Zalis, H. Kelm, H. J. Kruger, B. Sarkar, W. Kaim, *Organometallics* **2009**, *28*, 4196–4209.
[122] K. Osakada, T. Sakano, M. Horie, Y. Suzaki, *Coord. Chem. Rev.* **2006**, *250*, 1012–1022.
[123] M.-H. Desbois, D. Astruc, *New J. Chem.* **1989**, *13*, 595–600.
[124] J. K. Kochi, *J. Organomet. Chem.* **1986**, *300*, 139–272.
[125] T. J. Katz, *Adv. Organomet. Chem.* **1978**, *16*, 283–317 .
[126] Y. Chauvin, *Angew. Chem. Int. Ed.* **2006**, *45*, 3740; *Angew. Chem.* **2006**, *118*, 3824.
[127] D. Astruc, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 643–660; *Angew. Chem.* **1988**, *100*, 662.
[128] A. Studer, D. P. Curran, *Nat. Chem.* **2014**, *6*, 765–773.
[129] J.-M. Savéant, *Acc. Chem. Res.* **1980**, *13*, 323–329.
[130] G. A. Russell, *Adv. Phys. Org. Chem.* **1987**, *23*, 271–322.
[131] J. F. Bunnett, R. E. Zahler, *Chem. Rev.* **1951**, *49*, 273–412.
[132] N. Kornblum, *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 734–745; *Angew. Chem.* **1975**, *87*, 797.
[133] M. Chanon, *Acc. Chem. Res.* **1987**, *20*, 214–221.
[134] R. L. Rich, H. Taube, *J. Am. Chem. Soc.* **1954**, *76*, 2608–2611.
[135] K. Foo, E. Sella, I. Thome, M. D. Eastgate, P. S. Baran, *J. Am. Chem. Soc.* **2014**, *136*, 5279–5282.
[136] J. Elbert, J. Mersini, N. Vilbrandt, C. Lederle, M. Kraska, M. Gallei, B. Stühn, H. Plenio, M. Rehahn, *Macromolecules* **2013**, *46*, 4255.
[137] P. Neumann, H. Dib, A.-M. Caminade, E. Hey-Hawkins, *Angew. Chem. Int. Ed.* **2015**, *54*, 311–314; *Angew. Chem.* **2015**, *127*, 316.
[138] A. N. Nesmeyanov, N. A. Volkenau, I. N. Bolesova, *Tetrahedron Lett.* **1963**, *4*, 1725–1729.
[139] D. Astruc, *Tetrahedron* **1983**, *39*, 4027–4095.
[140] A. S. Abd-El-Aziz, S. Bernardin, *Coord. Chem. Rev.* **2000**, *203*, 219–267.
[141] J.-R. Hamon, D. Astruc, P. Michaud, *J. Am. Chem. Soc.* **1981**, *103*, 758–766.
[142] J. E. Sheats, M. D. Rausch, *J. Org. Chem.* **1970**, *35*, 3245–3249.
[143] B. Gloaguen, D. Astruc, *J. Am. Chem. Soc.* **1990**, *112*, 4607–4609.
[144] F. Moulines, D. Astruc, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1347–1349; *Angew. Chem.* **1988**, *100*, 1394.
[145] J.-L. Fillaut, J. Linares, D. Astruc, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2460–2462; *Angew. Chem.* **1994**, *106*, 2540.
[146] J. Ruiz, F. Ogliaro, J.-Y. Saillard, J.-F. Halet, F. Varret, D. Astruc, *J. Am. Chem. Soc.* **1998**, *120*, 11693–11705.
[147] M. V. Rajasekharan, M. V. Giesinsky, J. H. Ammeter, J.-R. Hamon, P. Michaud, D. Astruc, *J. Am. Chem. Soc.* **1982**, *104*, 2400–2407.
[148] C. Moinet, E. Roman, D. Astruc, *J. Electroanal. Chem.* **1981**, *121*, 241–253.
[149] J. C. Green, M. R. Kelly, M. P. Payne, D. Astruc, J.-R. Hamon, P. Michaud, *Organometallics* **1983**, *2*, 211–218.
[150] D. Astruc, E. Roman, J.-R. Hamon, *J. Am. Chem. Soc.* **1979**, *101*, 2240–2242.
[151] W. E. Geiger, *J. Am. Chem. Soc.* **1974**, *96*, 2632–2634.
[152] J. H. Ammeter, J. D. Swalen, *J. Chem. Phys.* **1972**, *57*, 678–682.
[153] C. Bossard, S. Rigaut, D. Astruc, M.-H. Delville, P. Delhaes, *J. Chem. Soc., Chem. Commun.* **1993**, 333–334.
[154] T. P. Gill, K. R. Mann, *Inorg. Chem.* **1983**, *22*, 1986–1991.
[155] D. Catheline, D. Astruc, *J. Organomet. Chem.* **1983**, *248*, C9–C12.
[156] D. Catheline, D. Astruc, *J. Organomet. Chem.* **1984**, *272*, 417–426.
[157] A. K. Diallo, J. Ruiz, D. Astruc, *Inorg. Chem.* **2010**, *49*, 1913–1920.
[158] J. Ruiz, M. Lacoste, D. Astruc, *J. Am. Chem. Soc.* **1990**, *112*, 5471–5483.
[159] J. F. Helling, D. M. Braitsch, *J. Am. Chem. Soc.* **1970**, *92*, 7207–7209.
[160] A. M. Madonik, D. Astruc, *J. Am. Chem. Soc.* **1984**, *106*, 2437–2439.
[161] R. Cataliotti, A. Foffani, S. Pignataro, *Inorg. Chem.* **1970**, *9*, 2594–2595.
[162] J. Zakrzewski, C. Giannotti, *J. Organomet. Chem.* **1990**, *388*, 175–179.
[163] K. Kowalski, *Coord. Chem. Rev.* **2010**, *254*, 1895–1917.
[164] O. J. Scherer, T. Bruck, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 59; *Angew. Chem.* **1987**, *99*, 59.
[165] C. Heindl, S. Reisinger, C. Schwarzmair, L. Rummel, A. V. Virovets, E. V. Peresypkina, M. Scheer, *Eur. J. Inorg. Chem.* **2016**, 743–753.
[166] E. Peresypkina, A. Virovets, M. Scheer, *Cryst. Growth Des.* **2016**, *16*, 2335–2341.
[167] F. S. Arimoto, A. C. Haven Jr., *J. Am. Chem. Soc.* **1955**, *77*, 6295.
[168] R. D. A. Hudson, *J. Organomet. Chem.* **2001**, *637*, 47–69.
[169] Neuse, E. W. J. Inorg, *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 3–32.
[170] C. E. J. Carraher, *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 121–146.
[171] A. S. Abd-El-Aziz, C. Agatemor, N. Etkin, *Macromol. Rapid Commun.* **2014**, *35*, 513–559.
[172] M. Hadadpour, J. Gwyther, I. Manners, P. J. Ragogna, *Chem. Mater.* **2015**, *27*, 3430–3440.
[173] D. A. Foucher, B. Z. Tang, I. Manners, *J. Am. Chem. Soc.* **1992**, *114*, 6246–6248.
[174] Y. Z. Ni, R. Rulkens, I. Manners, *J. Am. Chem. Soc.* **1996**, *118*, 4102–4114.
[175] M. Tanabe, G. W. M. Vandermeulen, W. Y. Chan, P. W. Cyr, L. Vanderark, D. A. Ryder, I. Manners, *Nat. Mater.* **2006**, *5*, 467–470.
[176] R. Rulkens, A. J. Lough, I. Manners, S. R. Lovelace, C. Grant, W. E. Geiger, *J. Am. Chem. Soc.* **1996**, *118*, 12683–12695.
[177] C. E. Boott, D. J. Lunn, I. Manners, *J. Polym. Sci., Part A* **2016**, *54*, 245–252.
[178] F. H. Schacher, P. A. Rupar, I. Manners, *Angew. Chem. Int. Ed.* **2012**, *51*, 7898–7921; *Angew. Chem.* **2012**, *124*, 8020.
[179] E. Boisselier, A. C. K. Shun, J. Ruiz, E. Cloutet, C. Belin, D. Astruc, *New J. Chem.* **2009**, *33*, 246–253.
[180] T. Hirao, M. Kurashina, K. Aramaki, H. Nishihara, *J. Chem. Soc., Dalton Trans.* **1996**, 2929–2933.

[181] J. B. Heilmann, M. Scheibitz, Y. Qin, A. Sundararaman, F. Jakle, T. Kretz, M. Bolte, H. W. Lerner, M. C. Holthausen, M. Wagner, *Angew. Chem. Int. Ed.* **2006**, *45*, 920–925; *Angew. Chem.* **2006**, *118*, 934.
[182] A. Alkan, A. Natanello, M. Wagner, H. Frey, F. R. Wurm, *Macromolecules* **2014**, *47*, 2242–2249.
[183] R. R. Schrock, *Acc. Chem. Res.* **1990**, *23*, 158–165.
[184] M. R. Buchmeiser, *Chem. Rev.* **2000**, *100*, 1565–1604.
[185] C. W. Bielawski, R. H. Grubbs, *Prog. Polym. Sci.* **2008**, *33*, 759–785.
[186] C. Deraedt, M. d'Halluin, D. Astruc, *Eur. J. Inorg. Chem.* **2013**, 4881–4908.
[187] A-C. Knall, C. Slugovc, in *Olefin Metathesis – Theory and Practice* (Ed.: K. Grela), Wiley, Hoboken, NJ, **2014**, pp. 269–284.
[188] M. S. Sanford, J. A. Love, R. H. Grubbs, *Organometallics* **2001**, *20*, 5314–5318.
[189] G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* **2010**, *110*, 1746–1787.
[190] A. S. Abd-El-Aziz, C. Agatemor, N. Etkin, *Macromol. Rapid Commun.* **2014**, *35*, 513–559.
[191] C. G. Hardy, J. Zhang, Y. Yan, L. Ren, C. Tang, *Prog. Polym. Sci.* **2014**, *39*, 1742–1796.
[192] Y. Zha, H. D. Thaker, R. R. Maddikeri, S. P. Gido, M. T. Tuominen, G. N. Tew, *J. Am. Chem. Soc.* **2012**, *134*, 14534–14541.
[193] L. Ren, J. Zhang, X. Bai, C. G. Hardy, K. D. Shimizu, C. Tang, *Chem. Sci.* **2012**, *3*, 580–583.
[194] Y. Yan, J. Y. Zhang, Y. L. Qiao, C. Tang, *Macromol. Rapid Commun.* **2014**, *35*, 254–259.
[195] H. Gu, A. Rapakousiou, P. Castel, N. Guidolin, N. Pinaud, J. Ruiz, D. Astruc, *Organometallics* **2014**, *33*, 4323–4335.
[196] A. Rapakousiou, C. Deraedt, H. Gu, L. Salmon, C. Belin, J. Ruiz, D. Astruc, *J. Am. Chem. Soc.* **2014**, *136*, 13995–13998.
[197] H. Gu, R. Ciganda, R. Hernández, P. Castel, P. Zhao, J. Ruiz, D. Astruc, *Macromolecules* **2015**, *48*, 6071–6076.
[198] H. Gu, R. Ciganda, P. Castel, A. Vax, D. Gregurec, J. Irigoyen, S. Moya, L. Salmon, P. Zhao, J. Ruiz, R. Hernández, D. Astruc, *Chem. Eur. J.* **2015**, *21*, 18177–18186.
[199] R. Ciganda, H. Gu, P. Castel, P. Zhao, J. Ruiz, R. Hernández, D. Astruc, *Macromol. Rapid Commun.* **2016**, *37*, 105–111.
[200] H. Gu, R. Ciganda, R. Hernández, P. Castel, A. Vax, P. Zhao, J. Ruiz, D. Astruc, *Polym. Chem.* **2016**, *7*, 2358–2371.
[201] H. Gu, R. Ciganga, S. Gatard, F. Lu, P. Zhao, J. Ruiz, D. Astruc, *J. Organomet. Chem.* **2016**, *813*, 95–102.
[202] I. Dragutan, V. Dragutan, H. Fischer, *J. Inorg. Organomet. Polym. Mater.* **2008**, *18*, 311–324.
[203] I. Dragutan, V. Dragutan, P. Filip, B. C. Simionescu, A. Demonceau, *Molecules* **2016**, *21*, 198.
[204] I. Dragutan, V. Dragutan, B. Siminescu, A. Demonceau, H. Fischer, *Beilstein J. Org. Chem.* **2015**, *11*, 2747–2762.
[205] R. H. Staff, M. Gallei, M. Mazurowski, M. Rehahn, R. Berger, K. Landfester, D. Crespy, *ACS Nano* **2012**, *6*, 9042.
[206] J. Elbert, M. Gallei, C. Rüttiger, A. Brunsen, H. Didzoleit, B. Stühn, M. Rehahn, *Organometallics* **2013**, *32*, 5873.
[207] K. Liu, C.-L. Ho, S. Aouba, Y.-Q. Zhao, Z.-H. Lu, S. Petrov, N. Coombs, P. Dube, H. E. Ruda, W.-Y. Wong, I. Manners, *Angew. Chem. Int. Ed.* **2008**, *47*, 1255; *Angew. Chem.* **2008**, *120*, 1275.
[208] Q. Dong, G. Li, C.-L. Ho, M. Faisal, C.-W. Leung, P. W.-T. Pong, K. Liu, B.-Z. Tang, I. Manners, W.-Y. Wong, *Adv. Mater.* **2012**, *24*, 1034.
[209] Q. Dong, G. Li, C.-L. Ho, C.-W. Leung, P. W.-T. Pong, I. Manners, W.-Y. Wong, *Adv. Funct. Mater.* **2014**, *24*, 857.
[210] J. Elbert, F. Krohm, C. Rüttiger, S. Kienle, H. Didzoleit, B. N. Balzer, T. Hugel, B. Stühn, M. Gallei, A. Brunsen, *Adv. Funct. Mater.* **2014**, *24*, 1591–1601.
[211] Q. Dong, G. Li, H. Wang, P. W.-T. Pong, C.-W. Leung, I. Manners, C.-L. Ho, H. Li, W.-Y. Wong, *J. Mater. Chem. C* **2015**, *3*, 734.
[212] J. Xiang, T.-K. Wang, Q. Zhao, W. Huang, C.-L. Ho, W.-Y. Wong, *J. Mater. Chem. C* **2016**, *4*, 921.
[213] Y. Yan, P. Pageni, M. P. Kabir, C. B. Tang, *Synlett* **2016**, *27*, 984–1005.
[214] M. F. Ni, N. Zhang, W. Xia, X. Wu, C. H. Yao, X. Liu, X. Y. Hu, C. Lin, L. Y. Wang, *J. Am. Chem. Soc.* **2016**, *138*, 6643–6649.
[215] K. S. Park, S. B. Schougaard, J. B. Goodenough, *Adv. Mater.* **2007**, *19*, 848.
[216] C. Su, L. Ji, L. Xu, X. Zhu, H. He, Y. Lv, M. Ouyang, C. Zhang, *RSC Adv.* **2015**, *5*, 14053.
[217] J. Xiang, R. Burges, B. Häupler, A. Wild, U. S. Schubert, C. L. Ho, W. Y. Wong, *Polymer* **2015**, *68*, 328.
[218] H. Zhong, G. Wang, Z. Song, X. Li, H. Tang, Y. Zhou, H. Zhan, *Chem. Commun.* **2014**, *50*, 6768.
[219] Y. Ding, Y. Zhao, G. Yu, *Nano Lett.* **2015**, *15*, 4108.
[220] S. M. Beladi-Mousavi, S. Sadaf, L. Walder, M. Gallei, C. Rüttiger, S. igler, C. E. Halbig, *Adv. En. Mater.* **2016**, DOI: 10.1002/aenm.201600108.
[221] P. D. Beer, E. J. Haye, *Coord. Chem. Rev.* **2003**, *240*, 167–189.
[222] O. N. Kadkin, Yu. G. Galyametdinov, *Russ. Chem. Rev.* **2012**, *81*, 675–699.
[223] N. H. Evans, P. D. Beer, *Angew. Chem. Int. Ed.* **2014**, *53*, 11716–11754; *Angew. Chem.* **2014**, *126*, 11908.
[224] N. H. Evans, P. D. Beer, *Org. Biomol. Chem.* **2011**, *9*, 92–100.
[225] G. T. Spence, P. D. Beer, *Acc. Chem. Res.* **2013**, *46*, 571–586; M. J. Langton, S. W. Robinson, I. Marques, P. D. Beer, *Acc. Chem. Res.* **2014**, *47*, 1935–1949.
[226] L. C. Gilday, S. W. Robinson, T. A. Barendt, M. J. Langton, B. R. Mullaney, P. D. Beer, *Chem. Rev.* **2015**, *115*, 7118–7195.
[227] M. J. Langton, C. J. Serpel, P. D. Beer, *Angew. Chem. Int. Ed.* **2016**, *55*, 1974–1987; *Angew. Chem.* **2016**, *128*, 2012.
[228] A. Caballero, F. Zapata, P. D. Beer, *Coord. Chem. Rev.* **2013**, *257*, 2434–2455.
[229] N. H. Evans, C. J. Serpel, N. G. White, P. D. Beer, *Chem. Eur. J.* **2011**, *17*, 12347–12354.
[230] N. G. White, P. D. Beer, *Beilstein J. Org. Chem.* **2012**, *8*, 6230–6237.
[231] F. Zapata, A. Caballero, A. Espinosa, A. Tarraga, P. Molina, *J. Org. Chem.* **2008**, *73*, 4034–4044.
[232] F. Oton, A. Espinosa, M. D. Velasco, P. Molina, *J. Org. Chem.* **2006**, *71*, 4590–4598.
[233] A. E. Kaifer, *Acc. Chem. Res.* **1999**, *32*, 62–71.
[234] C. M. Cardona, S. Mendoza, A. E. Kaifer, *Chem. Soc. Rev.* **2000**, *29*, 37–42.
[235] W. S. Jeon, K. Moon, S. H. Park, H. Chun, Y. H. Ko, J. Y. Lee, E. S. Lee, S. Samal, N. Selvapalam, M. V. Rekkarsky, Y. Inoue, A. E. Kaifer, K. Kim, *J. Am. Chem. Soc.* **2005**, *127*, 12984–12989.
[236] W. Li, A. E. Kaifer, *Organometallics* **2013**, *32*, 6091–6097.
[237] A. E. Kaifer, *Acc. Chem. Res.* **2014**, *47*, 2160–2167.
[238] M. L. H. Green, S. R. Marder, M. E. Thompson, J. A. Bandy, D. Bloor, P. V. Kolinsky, R. J. Jones, *Nature* **1987**, *330*, 6146.
[239] K. N. Jayaprakash, P. C. Ray, I. Matsuoka, M. M. Bhadbhade, V. G. Puranik, P. K. Das, H. Nishihara, A. Sarkar, *Organometallics* **1999**, *18*, 3851–3858.
[240] S. Barlow, H. E. Bunting, C. Ringham, J. C. Green, G. U. Bublitz, S. G. Boxer, S. R. Marder, *J. Am. Chem. Soc.* **1999**, *121*, 3715–3723.
[241] W.-Y. Wang, N.-N. Ma, S.-L. Sun, Y. Q. Qiu, *Phys. Chem. Chem. Phys.* **2014**, *16*, 4900–4910.
[242] C. Manzur, M. Fuentealba, J.-R. Hamon, D. Carrillo, *Coord. Chem. Rev.* **2010**, *254*, 765–780.
[243] A. Trujillo, M. Fuentealba, D. Carrillo, C. Manzur, I. Ledoux-Rak, J.-R. Hamon, J.-Y. Saillard, *Inorg. Chem.* **2010**, *49*, 2750–2764.
[244] S. Celedón, V. Dorcet, T. Roisnel, A. Singh, I. Ledoux-Rak, J.-R. Hamon, D. Carrillo, C. Manzur, *Eur. J. Inorg. Chem.* **2014**, 4984–4993.
[245] N. Novoa, T. Roisnel, P. Hamon, S. Kahlal, C. Manzur, H. M. Ngo, I. Ledoux-Rak, J.-Y. Saillard, D. Carrillo, J.-R. Hamon, *Dalton Trans.* **2015**, *44*, 18019–18037.
[246] J. Cisterna, V. Dorcet, C. Manzur, I. Ledoux-Rak, J.-R. Hamon, D. Carrillo, *Inorg. Chim. Acta* **2015**, *430*, 82–90.
[247] S. Celedón, M. Fuentealba, T. Roisnel, I. Ledoux-Rak, J.-R. Hamon, D. Carrillo, C. Manzur, *Eur. J. Inorg. Chem.* **2016**, 3012–3023.
[248] S. Fery-Forgues, B. Delavaut-Nicot, *J. Photochem. Photobiol. A* **2000**, *132*, 137–159.
[249] L. Xu, Y.-X. Wang, L.-J. Chen, H.-B. Yang, *Chem. Soc. Rev.* **2015**, *44*, 2148–2167.
[250] L. Barisic, M. Dropucic, V. Rapic, H. Pritzkow, S. I. Kirin, N. Metzler-Nolte, *Chem. Commun.* **2004**, 2004–2005.
[251] L. Barisic, M. Cakic, K. A. Mahmoud, Y. N. Liu, H. B. Kraatz, H. Pritzkow, S. I. Kirin, N. Metzler-Nolte, V. Rapic, *Chem. Eur. J.* **2006**, *12*, 4965–4980.
[252] V. Kovac, M. C. Semencic, I. Kodrin, S. Roca, V. Rapic, *Tetrahedron* **2013**, *69*, 10497–10506.
[253] C. Förster, M. Kovacevic, L. Barisic, V. Rapic, K. Heinze, *Organometallics* **2012**, *31*, 3683–3694.

[254] M. C. Semencic, V. Kovac, I. Kodrin, L. Barisic, V. Rapic, *Eur. J. Inorg. Chem.* **2015**, 112–113.
[255] V. Kovac, M. C. Semencic, K. Molcanov, I. Stabljic, D. Ivekovic, M. Zinic, V. Rapic, *Tetrahedron* **2012**, *68*, 7884–7891.
[256] R. Deschenaux, E. Serano, A.-M. Levelut, *Chem. Commun.* **1997**, 1577–1578.
[257] M. Even, B. Heinrich, D. Guillon, D. M. Guldi, M. Prato, R. Deschenaux, *Chem. Eur. J.* **2001**, *7*, 2595–2604.
[258] S. Campidelli, E. Vasquez, D. Milic, M. Prato, J. Barbera, D. M. Guldi, M. Marcaccio, D. Paolucci, F. Paolucci, R. Deschenaux, *J. Mater. Chem.* **2004**, *14*, 1266–1272.
[259] J. Brettar, T. Burgi, B. Donnio, D. Guillon, R. Klappert, T. Scharf, R. Deschenaux, *Adv. Funct. Mater.* **2006**, *16*, 260–267.
[260] B. Donnio, *Inorg. Chim. Acta* **2014**, *409*, 53–67.
[261] J. F. Smalley, S. B. Sachs, C. E. D. Chidsey, *J. Am. Chem. Soc.* **2004**, *126*, 14620–14630.
[262] C. Fabre, *Acc. Chem. Res.* **2010**, *43*, 1509–1518.
[263] C. Bucher, C. H. Devillers, J.-C. Moutet, G. Royal, *Coord. Chem. Rev.* **2009**, *253*, 21–36.
[264] H. Guttmann, US Patent 5386804 A, **1995**; http://www.google.com/patents/US5386804.
[265] R. Sen, A. Govindaraj, C. N. R. Rao, *Chem. Phys. Lett.* **1997**, *267*, 276–280.
[266] R. Q. Yu, L. W. Chen, Q. P. Liu, *Chem. Mater.* **1998**, *10*, 718–722.
[267] R. Andrews, D. Jacques, A. M. Rao, F. Derbyshire, D. Qian, X. Fan, E. C. Dickey, J. Chen, *Chem. Phys. Lett.* **1999**, *303*, 467–474.
[268] A. Barreiro, S. Hampel, M. H. Rümmeli, C. Kramberger, A. Grüneis, K. Biedermann, A. Leonhardt, T. Gemming, B. Büchner, A. Bachtold, T. Pichler, *J. Phys. Chem. B* **2006**, *110*, 20973–20977.
[269] J. Guo, Y. He, S. L. Wang, F. S. Boi, *Carbon* **2016**, *102*, 372–382.
[270] E. Peris, *Coord. Chem. Rev.* **2004**, *248*, 279–297.
[271] Y. Yu, A. D. Bond, P. W. Leonard, U. J. Lorenz, T. V. Timofeeva, K. P. C. Vollhardt, G. D. Whitener, A. A. Yakovenko, *Chem. Commun.* **2006**, 2572–2574.
[272] A. K. Diallo, J.-C. Daran, F. Varret, J. Ruiz, D. Astruc, *Angew. Chem. Int. Ed.* **2009**, *48*, 3141–3145; *Angew. Chem.* **2009**, *121*, 3187.
[273] A. K. Diallo, C. Absalon, J. Ruiz, D. Astruc, *J. Am. Chem. Soc.* **2011**, *133*, 629–641.
[274] S. Nlate, J. Ruiz, J.-C. Blais, D. Astruc, *Chem. Commun.* **2000**, 417–418.
[275] J. B. Flanagan, A. Marcel, A. J. Bard, F. C. Anson, *J. Am. Chem. Soc.* **1978**, *100*, 4248–4253.
[276] R. J. LeSuer, W. E. Geiger, *Angew. Chem. Int. Ed.* **2000**, *39*, 248–250; *Angew. Chem.* **2000**, *112*, 254.
[277] F. Barrière, N. Camine, W. E. Geiger, *J. Am. Chem. Soc.* **2002**, *124*, 7262–7263.
[278] F. Barrière, W. E. Geiger, *J. Am. Chem. Soc.* **2006**, *128*, 3980–3989.
[279] F. Barrière, W. E. Geiger, *Acc. Chem. Res.* **2010**, *43*, 1030–1039.
[280] P. Jutzi, B. Kleinebekel, *J. Organomet. Chem.* **1997**, *545–546*, 573–576.
[281] H. Fink, N. J. Long, A. J. Martin, G. Opromolla, A. J. P. White, D. J. Williams, P. Zanello, *Organometallics* **1997**, *16*, 2646–2650.
[282] B. Grossmann, J. Heinze, E. Hertweck, F. H. Köhler, H. Nöth, H. Schwenk, M. Spiegler, W. Wachter, B. Weber, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 387–389; *Angew. Chem.* **1997**, *109*, 384.
[283] D. E. Herbert, J. B. Gilroy, W. Y. Chan, L. Chabanne, A. Staubitz, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2009**, *131*, 14958–14968.
[284] M. S. Inkpen, S. Scheerer, M. Linseis, A. J. P. White, R. F. Winter, T. Albrecht, N. J. Long, *Nat. Chem.* **2016**, DOI: 10.1038/nchm.2553.
[285] J.-L. Fillaut, J. Linares, D. Astruc, *Angew. Chem. Int. Ed. Engl.* **1993**, *33*, 2460–2462; *Angew. Chem.* **1993**, *105*, 2540.
[286] F. Moulines, L. Djakovitch, R. Boese, B. Gloaguen, W. Thiel, J.-L. Fillaut, M.-H. Delville, D. Astruc, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1075–1077; *Angew. Chem.* **1993**, *105*, 1132.
[287] C. M. Casado, I. Cuadrado, B. Alonso, M. Moran, J. Losada, V. Belsky, *J. Am. Chem. Soc.* **1997**, *119*, 7613–7614.
[288] C. Valério, J.-L. Fillaut, J. Ruiz, J. Guittard, J.-C. Blais, D. Astruc, *J. Am. Chem. Soc.* **1997**, *119*, 2588–2589.
[289] C. M. Casado, B. Gonzales, I. Cuadrado, B. Alonso, M. Moran, J. Losada, *Angew. Chem. Int. Ed.* **2000**, *39*, 2135; *Angew. Chem.* **2000**, *112*, 2219.
[290] C. M. Casado, I. Cuadrado, M. Moran, B. Alonso, B. Garcia, B. Gonzales, J. Losada, *Coord. Chem. Rev.* **1999**, *185–186*, 53–79.
[291] S. H. Hwang, C. D. Shreiner, C. N. Moorefield, G. R. Newkome, *New J. Chem.* **2007**, *31*, 1027–1038.
[292] F. J. Martinez, B. Gonzales, B. Alonso, J. Losada, M. P. Garcia-Armanda, C. M. Casado, *J. Inorg. Organomet. Polym. Mater.* **2008**, *18*, 51–58.
[293] C. M. Casado, B. Alonso, J. Losada, M. P. Garcia-Armanda, in *Designing Dendrimers* (Eds.: S. Campagna, P. Ceroni, F. Puntoriero), Wiley, Hoboken, NJ, **2012**, pp. 219–262.
[294] D. Astruc, *Nat. Chem.* **2012**, *4*, 255–267.
[295] A. Labande, J. Ruiz, D. Astruc, *J. Am. Chem. Soc.* **2002**, *124*, 1782–1789.
[296] M.-C. Daniel, J. Ruiz, S. Nlate, J.-C. Blais, D. Astruc, *J. Am. Chem. Soc.* **2003**, *125*, 2617–2628.
[297] M. Yamada, H. Nishihara, *Chem. Commun.* **2002**, 2578–2579.
[298] M. Yamada, H. Nishihara, *C. R. Chim.* **2003**, *6*, 919–934.
[299] A. Rapakousiou, C. Deraedt, J. Irigoyen, Y. Wang, N. Pinaud, L. Samon, J. Ruiz, S. Moya, D. Astruc, *Inorg. Chem.* **2015**, *54*, 2284–2299.
[300] C. Ornelas, J. Ruiz, E. Cloutet, S. Alves, D. Astruc, *Angew. Chem. Int. Ed.* **2007**, *46*, 872–877; *Angew. Chem.* **2007**, *119*, 890.
[301] R. Djeda, A. Rapakousiou, L. Liang, N. Guidolin, J. Ruiz, D. Astruc, *Angew. Chem. Int. Ed.* **2010**, *49*, 8152–8156; *Angew. Chem.* **2010**, *122*, 8328.
[302] A. Caballero, F. Zapata, L. Gonzales, P. Molina, I. Alkorta, J. Elguro, *Chem. Commun.* **2014**, *50*, 4680–4682.
[303] P. R. Ashton, V. Balzani, M. Clemente-Leon, B. Colonna, A. Credi, N. Jayaraman, F. M. Raymo, J. F. Stoddart, M. Venturi, *Chem. Eur. J.* **2002**, *8*, 673–684.
[304] A. E. Kaifer, *Eur. J. Inorg. Chem.* **2007**, 5015–5027.
[305] C. Ornelas, J. Ruiz, C. Belin, D. Astruc, *J. Am. Chem. Soc.* **2009**, *131*, 590–601.
[306] A. Wang, C. Ornelas, D. Astruc, P. Hapiot, *J. Am. Chem. Soc.* **2009**, *131*, 6652–6653.
[307] S. Lhenry, J. Jalkh, Y. Leroux, J. Ruiz, R. Ciganda, D. Astruc, P. Hapiot, *J. Am. Chem. Soc.* **2014**, *136*, 17950–17953.
[308] N. Vilà, E. André, R. Ciganda, J. Ruiz, D. Astruc, A. Walcarius, *Chem. Mater.* **2016**, *28*, 2511–2514.
[309] K. Diallo, C. Ornelas, L. Salmon, J. Ruiz, D. Astruc, *Angew. Chem. Int. Ed.* **2007**, *46*, 8644–8648; *Angew. Chem.* **2007**, *119*, 8798.
[310] I. P. Beletskaya, A. V. Cheprakov, *J. Organomet. Chem.* **2004**, *689*, 4055.
[311] C. Deraedt, D. Astruc, *Acc. Chem. Res.* **2014**, *47*, 494–503.
[312] J. G. de Vries, *Dalton Trans.* **2006**, 421–429.
[313] F. Lu, D. Astruc, *Eur. J. Inorg. Chem.* **2015**, 5595–5600.
[314] G. Gasser, I. Ott, N. Metzler-Nolte, *J. Med. Chem.* **2011**, *54*, 3–25.
[315] C. Ornelas, *New J. Chem.* **2011**, *35*, 1973–1985.
[316] P. Koepf-Maier, H. Köpf, *Chem. Rev.* **1987**, *87*, 1137–1152.
[317] *Bioorganometallics* (Ed.: G. Jaouen), Wiley-VCH, Weinheim, **2005**.
[318] "Medicinal Organometallic Chemistry" (Eds.: G. Jaouen, N. Metzler-Nolte), in *Topics in Organometallic Chemistry*, Springer, Berlin, **2010**.
[319] *Biorganometallic Chemistry: Applications in Drug Discovery, Biocatalysis and Imaging* (Eds.: G. Jaouen, M. Salmain), Wiley-VCH, Weinheim, **2015**.
[320] M. F. R. Fouda, M. M. Abd-Elzaher, R. A. Abdelsamaia, A. A. Labib, *Appl. Organomet. Chem.* **2007**, *21*, 613–625.
[321] D. Astruc, *C. R. Acad. Sci.* **1996**, *322*, 757–766.
[322] A. E. G. Cass, G. Davies, G. D. Francis, H. A. O. Hill, W. J. Aston, J. Higgins, E. V. Plotkin, L. D. L. Scott, A. P. F. Turner, *Anal. Chem.* **1984**, *56*, 667–671.
[323] A. Heller, B. Feldman, *Chem. Rev.* **2008**, *108*, 2482–2505.
[324] J. Wang, *Chem. Rev.* **2008**, *108*, 814–825.
[325] E.-H. Yoo, S.-Y. Lee, *Sensors* **2010**, *10*, 4558–4576.
[326] C. Biot, G. Glorian, A. Maciejewski, J. S. Brocard, O. Domarle, G. Blampain, P. Millet, A. J. George, H. Abessolo, D. Dive, J. Lebibi, *J. Med. Chem.* **1997**, *40*, 3715–3718.
[327] T. Vausselin, N. Calland, S. Belouzard, V. Descamp, F. Douam, F. Helle, C. François, D. Lavilette, G. Duverlie, A. Wahid, L. Fénéant, L. Cosquerel, Y. Guérardel, C. Wyshoswski, C. Biot, J. Dubisson, *Hepatology* **2013**, *58*, 86–97.
[328] V. J. Fiorina, R. J. Dubois, S. Brynes, *J. Med. Chem.* **1978**, *21*, 393–395.
[329] P. Köpf-Maier, H. Köpf, E. W. Neuse, *J. Cancer Res.* **1984**, *108*, 336–340.
[330] D. Osella, M. Ferrali, P. Zanello, F. Lashi, M. Fontani, C. Nervi, G. Cavigiolo, *Inorg. Chim. Acta* **2000**, *306*, 42–48.
[331] E. W. Neuse, *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 3–32.
[332] L. Snegur, Y. S. Nekrasov, N. S. Sergeeva, Z. V. Zhilina, V. V. Gumeniuyk, Z. A. Starikova, A. A. Simenel, N. B. Morozova, I. K. Sviridova, V. N. Babin, *Appl. Organomet. Chem. Appl. Organomet.* **2008**, *22*, 139–147.

[333] A. A. Simenel, E. A. Morozova, L. V. Snegur, S. I. Zykova, V. V. Kachala, L. A. Ostrovskaya, N. V. Bluchterova, M. M. Fomina, *Appl. Organomet. Chem.* **2009**, *23*, 219–224; B. Long, S. Liang, D. Xin, Y. Yang, J. Xiang, *Eur. J. Med. Chem.* **2009**, *44*, 2572–2576.
[334] A. D. S. Krishna, G. Panda, A. K. Kondapi, *Arch. Biochem. Biophys.* **2005**, *438*, 206–216.
[335] S. Top, J. Tang, A. Vessières, D. Carrez, C. Provot, G. Jaouen, *Chem. Commun.* **1996**, 955–956.
[336] S. Top, A. Vessieres, G. Leclercq, J. Quivy, J. Tang, J. Vaissermann, G. Jaouen, *Chem. Eur. J.* **2003**, *9*, 5223–5236.
[337] E. A. Hillard, A. Vessières, L. Thouin, G. Jaouen, C. Amatore, *Angew. Chem. Int. Ed.* **2006**, *45*, 285–290; *Angew. Chem.* **2006**, *118*, 291.
[338] E. A. Hillard, A. Vessières, G. Jaouen, *Top. Organomet. Chem.* **2010**, *32*, 716–724.
[339] G. Jaouen, A. Vessières, S. Top, *Chem. Soc. Rev.* **2015**, *44*, 8802–8817.
[340] A. P. Ferreira, J. L. F. da Silva, M. T. Duarte, M. F. M. da Piedade, M. P. Robalo, S. G. Harjivan, C. Marzano, V. Gandin, M. M. Marques, *Organometallics* **2009**, *28*, 5412–5423.
[341] J. Manosroi, K. Rueanto, K. Boonpisuttinant, W. Manosroi, C. Biot, H. Akazawa, T. Akihisha, W. Issarangporn, A. Manosroi, *J. Med. Chem.* **2010**, *53*, 3937–3943.
[342] R. P. Paitandi, R. K. Gupta, R. S. Singh, G. Sharma, B. Koch, D. S. Pandey, *Eur. J. Med. Chem.* **2014**, *84*, 17–29.
[343] J. Tauchman, G. Süss-Fink, P. Stepnicka, O. Zava, P. J. Dyson, *J. Organomet. Chem.* **2013**, *723*, 233–238.
[344] A. A. Altaf, B. Lal, A. Badshah, *J. Mol. Struct.* **2016**, *1113*, 162–170.
[345] J. Tian, J. Chen, C. C. Ge, X. Liu, J. L. He, P. H. Ni, Y. Pan, *Bioconjugate Chem.* **2016**, *27*, 1518–1524.
[346] A. Wieczorek, A. Blauz, J. Zakrewski, B. Rychlik, D. Plazuk, *ACS Med. Chem. Lett.* **2016**, *7*, 612–617.
[347] J. K. Muenzner, A. Ahmad, M. Rothemund, S. Schrufer, S. Padhye, F. H. Sarkar, R. Schobert, B. Biersack, *Appl. Organomet. Chem.* **2016**, *30*, 441–445.
[348] T. Noyhouzer, C. L'Homme, I. Beaulieu, *Langmuir* **2016**, *32*, 4169–4178.
[349] A. Hottin, A. Scadolera, L. Duca, D. W. Wright, G. J. Davies, J. B. Behr, *Bioorg. Med. Chem. Lett.* **2016**, *26*, 1546–1549.
[350] J. F. Arambula, R. McCall, K. J. Sidoran, D. Magda, N. A. Mitchel, C. W. Bielawski, V. M. Lynch, J. L. Sessler, K. Arumugam, *Chem. Sci.* **2016**, *7*, 1245–1256.
[351] C. Ornelas, *Macromol. Chem. Phys.* **2016**, *217*, 149–174.
[352] Q. P. Duan, Y. Cao, Y. Li, X. Y. Hu, T. X. Xiao, C. Lin, Y. Pan, L. Y. Wang, *J. Am. Chem. Soc.* **2013**, *135*, 10542–10549.
[353] M. T. Islam, S. P. Best, J. D. Bourke, L. J. Tantau, C. Q. Tran, F. Wang, C. T. Chantler, *J. Phys. Chem. C* **2016**, *120*, 9399–9418.
[354] A. Tanushi, T. Kusamoto, Y. Hattori, K. Takada, H. Nishihara, *J. Am. Chem. Soc.* **2015**, *137*, 6448–6451.
[355] T. Kusamoto, K. Takada, R. Sakamoto, S. Kume, H. Nishihara, *Inorg. Chem.* **2012**, *51*, 12102–12113.
[356] P. D. Beer, P. A. Gale, *Angew. Chem. Int. Ed.* **2001**, *40*, 486–516; *Angew. Chem.* **2001**, *113*, 502.
[357] P. Steffen, C. Unkelbach, M. Christmann, W. Hiller, C. Strohmann, *Angew. Chem. Int. Ed.* **2013**, *52*, 9836–9840.

Received: August 9, 2016
Published Online: October 5, 2016