1
Iron Complexes in Organic Chemistry

Ingmar Bauer and Hans-Joachim Knölker

1.1
Introduction

Catalysis is an important field in both academic and industrial research because it leads to more efficient reactions in terms of energy consumption and waste production. The common feature of these processes is a catalytically active species which forms reactive intermediates by coordination of an organic ligand and thus decreases the activation energy. Formation of the product should occur with regeneration of the catalytically active species. The efficiency of the catalyst can be described by its turnover number, providing a measure of how many catalytic cycles are passed by one molecule of catalyst.

For efficient regeneration, the catalyst should form only labile intermediates with the substrate. This concept can be realized using transition metal complexes because metal–ligand bonds are generally weaker than covalent bonds. The transition metals often exist in different oxidation states with only moderate differences in their oxidation potentials, thus offering the possibility of switching reversibly between the different oxidation states by redox reactions.

Many transition metals have been applied as catalysts for organic reactions [1]. So far, iron has not played a dominant role in catalytic processes. Organoiron chemistry was started by the discovery of pentacarbonyliron in 1891, independently by Mond [2] and Berthelot [3]. A further milestone was the report of ferrocene in 1951 [4]. Iron catalysis came into focus by the Reppe synthesis [5]. Kochi and coworkers published in 1971 their results on the iron-catalyzed cross-coupling of Grignard reagents with organic halides [6]. However, cross-coupling reactions became popular by using the late transition metals nickel and palladium. More recently, the increasing number of reactions using catalytic amounts of iron complexes indicates a renaissance of this metal in catalysis. This chapter describes applications of iron complexes in organic chemistry and thus paves the way for an understanding of iron catalysis.

Iron Catalysis in Organic Chemistry. Edited by Bernd Plietker

ISBN: 978-3-527-31927-5

1.2 General Aspects of Iron Complex Chemistry

1.2.1 Electronic Configuration, Oxidation States, Structures

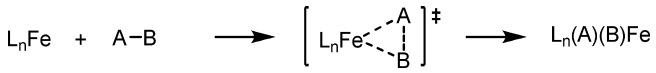
In complexes iron has an electronic configuration of $[Ar]4s^0 3d^8$. The most common oxidation states for iron are +2 and +3. Moreover, the oxidation states +6, 0, −1 and −2 are of importance. In contrast to osmium, iron never reaches its potential full oxidation state of +8 as a group VIII element. In air, most iron(II) compounds are readily oxidized to their iron(III) analogs, which represent the most stable and widespread iron species. For iron(II) complexes ($[Ar]4s^0 3d^6$) a coordination number of six with an octahedral ligand sphere is preferred. Iron(III) ($[Ar]4s^0 3d^5$) can coordinate three to eight ligands and often exhibits an octahedral coordination. Iron(III) generally is a harder Lewis acid than iron(II) and thus binds to hard Lewis bases. Iron(0) mostly coordinates five or six ligands with trigonal bipyramidal and octahedral geometry. Iron(–II) is tetrahedrally coordinated. Iron in low oxidation states is most interesting for organometallic chemistry and in particular for iron-catalyzed reactions because they can form more reactive complexes than their iron(II) and iron(III) counterparts. Therefore, iron(0) and iron(–II) compounds are favored for iron catalysis. Iron carbonyl complexes are of special interest due to their high stability with an iron(0) center capable of coordinating complex organic ligands, which represents the basis for organoiron chemistry.

1.2.2 Fundamental Reactions

The following fundamental reactions play a key role in organo-transition metal chemistry: halogen–metal exchange, ligand exchange, insertion, haptotropic migration, transmetallation, oxidative addition, reductive elimination, β-hydride elimination and demetallation. Generally, several of these reactions proceed sequentially to form a catalytic cycle. No stable product should be generated, as this would interrupt the catalytic cycle by preventing the subsequent step.

Oxidative addition generally increases the oxidation state of the metal by two units and, based on the common oxidation states of iron, leads from iron(0) to iron(II) or iron(–II) to iron(0). The former represents the most widespread system for iron catalysis in organic synthesis but the latter also has enormous potential for applications (see Section 1.4).

Oxidative additions are frequently observed with transition metal d^8 systems such as iron(0), osmium(0), cobalt(I), rhodium(I), iridium(I), nickel(II), palladium(II) and platinum(II). The reactivity of d^8 systems towards oxidative addition increases from right to left in the periodic table and from top to down within a triad. The concerted mechanism is most important and resembles a concerted cycloaddition in organic chemistry (Scheme 1.1). The reactivity of metal complexes is influenced by their



Scheme 1.1

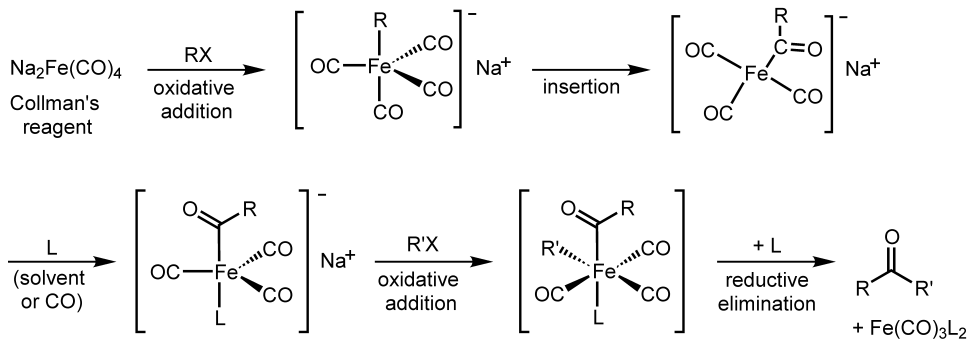
ligand sphere. Thus, strong σ-donor ligands and more poor π-acceptor ligands favor the oxidative addition due to increased electron density at the metal.

Reaction of the nucleophilic Collman's reagent ($Na_2Fe[CO]_4$) with two alkyl halides affords ketones via successive oxidative additions (Scheme 1.2) [7]. However, no catalytic cycle is achieved because the reaction conditions applied do not lead to regeneration of the reagent.

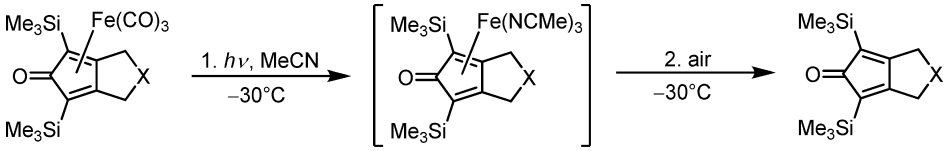
The reductive elimination eventually releases the newly formed organic product in a concerted mechanism. In the course of this process, the electron count is reduced by two. Iron has a great tendency for coordinative saturation, which in general does not favor processes such as ligand dissociation and reductive elimination. This aspect represents a potential limiting factor for catalytic reactions using iron.

Another important reaction typically proceeding in transition metal complexes is the insertion reaction. Carbon monoxide readily undergoes this process. Therefore, the insertion reaction is extremely important in organoiron chemistry for carbonylation of alkyl groups to aldehydes, ketones (compare Scheme 1.2) or carboxylic acid derivatives. Industrially important catalytic processes based on insertion reactions are hydroformylation and alkene polymerization.

Many metal-mediated reactions do not release the organic product by elimination but generate a stable transition metal complex, which prohibits a catalytic cycle. This is generally observed for diene–iron complexes which provide the free ligand only after removal of the metal by demetallation. Demetallation can be achieved using harsh oxidative conditions, which destroy the metal complex to give inert iron oxides. However, such conditions may lead to the destruction of sensitive organic ligands. In these cases, milder demetallation procedures are required to obtain the free ligand. For example, the demetallation has been a limiting factor for application of the

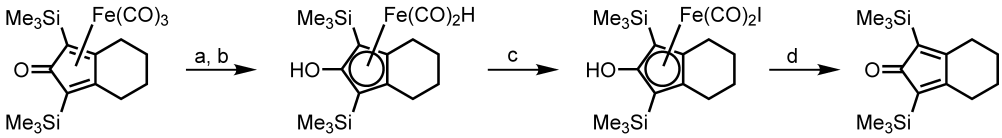


Scheme 1.2



X = CH_2, $(CH_2)_2$, $C(COOMe)_2$, S, O, NR

Scheme 1.3



a) 1M NaOH/THF (1/2); b) H_3PO_4; c) $C_5H_{11}I$; d) air, daylight, Et_2O/THF, $Na_2S_2O_3$, Celite®

Scheme 1.4

iron-mediated [2 + 2 + 1]-cycloaddition. The demetallation of tricarbonyl(η^4-cyclopentadienone)iron complexes using trimethylamine *N*-oxide provides low yields. Photolytically induced ligand exchange of carbon monoxide by the poor π-accepting acetonitrile leads to intermediate very labile tri(acetonitrile)iron complexes. Demetallation by bubbling of air through the solution at low temperature affords the free ligands in high yields (Scheme 1.3) [8].

A further novel method for demetallation provides even higher yields. Hieber-type reaction of the tricarbonyl(η^4-cyclopentadienone)iron complex with sodium hydroxide to the corresponding hydride complex followed by ligand exchange with iodopentane affords an intermediate iodoiron complex, which is readily demetallated in the presence of air and daylight at room temperature (Scheme 1.4) [9]. Combining steps a–c in a one-pot procedure without isolation of the intermediate hydride complex gave yields of up to 98%.

These examples demonstrate that ligand exchange of carbon monoxide by poor π-acceptor ligands provides, due to decreased back-bonding, labile complexes which can be demetallated under mild reaction conditions, providing the corresponding free ligands in high yields.

1.3 Organoiron Complexes and Their Applications

In order to understand catalytic systems based on iron, the chemistry of organoiron complexes is briefly described and their reactivity is demonstrated. A comprehensive summary of the applications of iron compounds in organic synthesis has been given by Pearson [7].

1.3.1
Binary Carbonyl–Iron Complexes

Iron forms three stable homoleptic complexes with carbon monoxide, pentacarbonyliron ($Fe[CO]_5$), nonacarbonyldiiron ($Fe_2[CO]_9$) and dodecacarbonyltriiron ($Fe_3[CO]_{12}$) (Figure 1.1).

Pentacarbonyliron is a stable 18-electron complex of trigonal-bipyramidal geometry and represents the primary source of most organoiron complexes. Nonacarbonyldiiron is prepared in a photolytic reaction from pentacarbonyliron. Dodecacarbonyltriiron can be obtained from nonacarbonyldiiron by a thermal reaction. Both, nonacarbonyldiiron and dodecacarbonyltriiron, contain metal–metal bonds. They are slowly degraded to give pyrophoric iron and therefore should be handled with care.

Iron carbonyls have been used in stoichiometric and catalytic amounts for a variety of transformations in organic synthesis. For example, the isomerization of 1,4-dienes to 1,3-dienes by formation of tricarbonyl(η^4-1,3-diene)iron complexes and subsequent oxidative demetallation has been applied to the synthesis of 12-prostaglandin PGC_2 [10]. The photochemically induced double bond isomerization of allyl alcohols to aldehydes [11] and allylamines to enamines [12, 13] can be carried out with catalytic amounts of iron carbonyls (see Section 1.4.3).

Iron carbonyls also mediate the cycloaddition reaction of allyl equivalents and dienes. In the presence of nonacarbonyldiiron α,α′-dihaloketones and 1,3-dienes provide cycloheptenes (Scheme 1.5) [14, 15]. Two initial dehalogenation steps afford a reactive oxoallyliron complex which undergoes a thermally allowed concerted [4 + 3]-cycloaddition with 1,3-dienes. The 1,3-diene system can be incorporated in cyclic or heterocyclic systems (furans, cyclopentadienes and, less frequently, pyrroles). Noyori and coworkers applied this strategy to natural product synthesis, e.g. α-thujaplicin and β-thujaplicin [14, 16].

The reducing ability of iron(0) complexes has been exploited for functional group interconversion, for example reduction of aromatic nitro compounds to amines by dodecacarbonyltriiron [17].

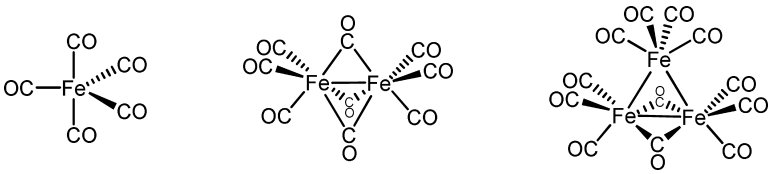
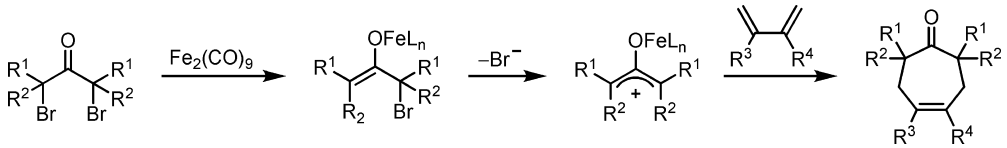


Figure 1.1 Homoleptic ironcarbonyl complexes.

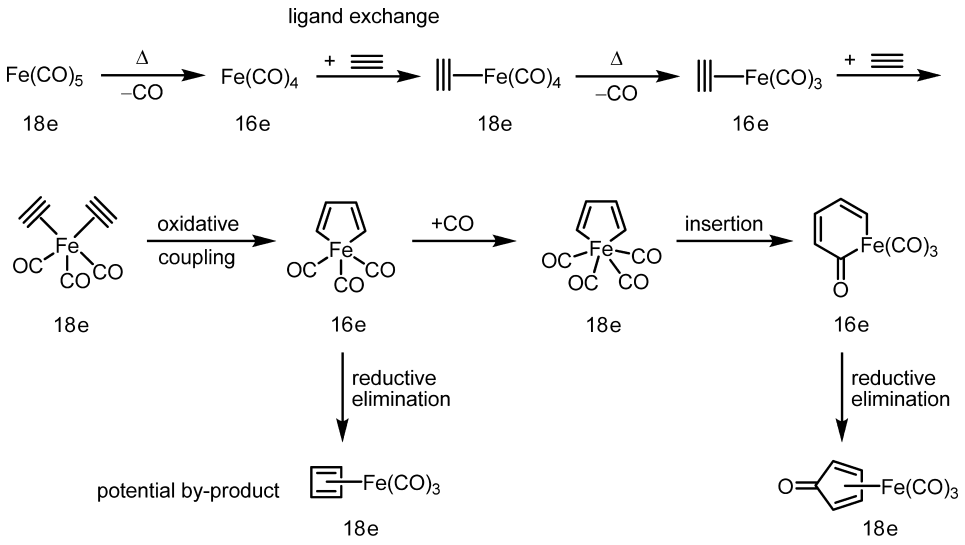


Scheme 1.5

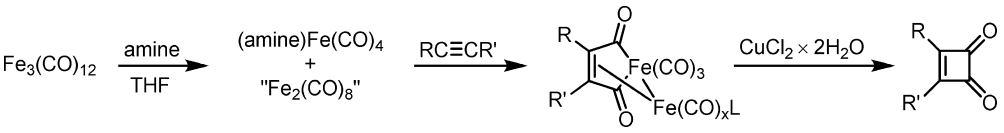
Addition of nucleophiles to a carbon monoxide ligand of pentacarbonyliron provides anionic acyliron intermediates which can be trapped by electrophiles (H^+ or R–X) to furnish aldehydes or ketones [18]. However, carbonyl insertion into alkyl halides using iron carbonyl complexes is more efficiently achieved with disodium tetracarbonylferrate (Collman's reagent) and provides unsymmetrical ketones (Scheme 1.2) [19, 20]. Collman's reagent is extremely sensitive towards air and moisture, but offers a great synthetic potential as carbonyl transfer reagent. It can be prepared by an *in situ* procedure starting from $Fe(CO)_5$ and Na–naphthalene [20].

The reaction of two alkynes in the presence of pentacarbonyliron affords via a [2 + 2 + 1]-cycloaddition tricarbonyl(η^4-cyclopentadienone)iron complexes (Scheme 1.6) [5, 21–23]. An initial ligand exchange of two carbon monoxide ligands by two alkynes generating a tricarbonyl[bis(η^2-alkyne)]iron complex followed by an oxidative cyclization generates an intermediate ferracyclopentadiene. Insertion of carbon monoxide and subsequent reductive elimination lead to the tricarbonyl(η^4-cyclopentadienone)iron complex. These cyclopentadienone-iron complexes are fairly stable but can be demetallated to their corresponding free ligands (see Section 1.2.2). The [2 + 2 + 1]-cycloaddition requires stoichiometric amounts of iron as the final 18-electron cyclopentadienone complex is stable under the reaction conditions.

The iron-mediated [2 + 2 + 1]-cycloaddition to cyclopentadienones has been successfully applied to the synthesis of corannulene [24] and the yohimbane alkaloid (±)-demethoxycarbonyldihydrogambirtannine [25]. A [2 + 2 + 1]-cycloaddition of an alkene, an alkyne and carbon monoxide mediated by pentacarbonyliron, related to the well-known Pauson–Khand reaction [26], has also been described to afford cyclopentenones [27].



Scheme 1.6



Scheme 1.7

A double insertion of carbon monoxide has been observed for the amine-induced reaction of alkynes with dodecacarbonyltriiron leading to cyclobutenediones (Scheme 1.7) [28].

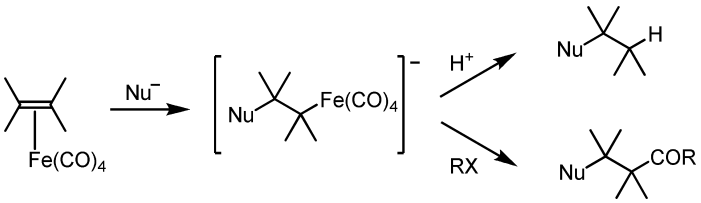
In the presence of an excess of a primary amine, this reaction has been applied to the synthesis of cyclic imides [29].

1.3.2
Alkene–Iron Complexes

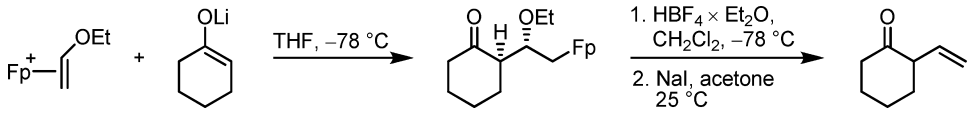
Neutral η^2-alkene–tetracarbonyliron complexes can be prepared from the corresponding alkene and nonacarbonyldiiron via a dissociative mechanism. The organic ligand in the alkene–iron complex is more easily attacked by nucleophiles than the corresponding free alkene due to the acceptor character of the tetracarbonyliron fragment. The reaction principle is demonstrated in Scheme 1.8 [30].

Malonate anions react with the η^2-ethylene–$Fe(CO)_4$ complex to afford after demetallation ethyl malonate derivatives. Reaction of nucleophiles with tetracarbonyliron-activated α,β-unsaturated carbonyl compounds leads after protonation of the intermediate alkyl–$Fe(CO)_4$ anions to the products of Michael addition.

Cationic alkene complexes of the type $[\eta^2$-alkene–Fp$]^+$ [Fp = $CpFe(CO)_2$] are available by reaction of the alkenes with $CpFe(CO)_2Br$. Alternatively, several indirect routes to these complexes are provided by using $CpFe(CO)_2Na$. Both reagents can be prepared from the dimer $[Cp(CO)_2Fe]_2$. The Fp fragment serves as protecting group for alkenes and tolerates bromination and hydrogenation of other double bonds present in the molecule. Due to their positive charge, $[\eta^2$-alkene–Fp$]^+$ complexes react with a wide range of nucleophiles such as enamines, enolates, silyl enol ethers, phosphines, thiols and amines. The addition proceeds stereoselectively with the nucleophile approaching *anti* to the Fp group, but often shows poor regioselectivity. This drawback is overcome by using vinyl ether complexes, which are attacked by nucleophiles exclusively at the alkoxy-substituted carbon (Scheme 1.9). The intermediate alkyl–Fp complexes undergo elimination of alcohol and demetallation.



Scheme 1.8



Scheme 1.9

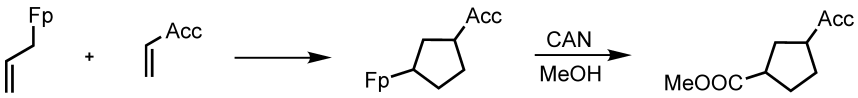
Thus, $[\eta^2$-alkene–Fp$]^+$ complexes represent useful cationic synthons for the vinylation of enolates [31].

Related [alkyne–Fp]$^+$ complexes can be obtained by ligand exchange of [isobutylene–Fp]$^+$ complexes with alkynes [32].

1.3.3
Allyl– and Trimethylenemethane–Iron Complexes

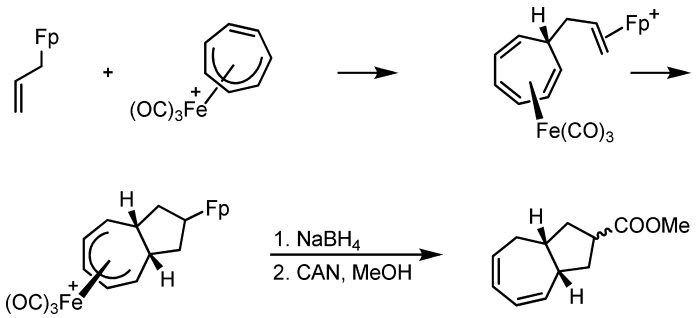
Allyl complexes of the type η^1-allyl–Fp are prepared by reaction of $[Cp(CO)_2Fe]^-Na^+$ with allyl halides or, alternatively, by deprotonation of $[\eta^2$-alkene–Fp$]^+$ complexes. The most important reaction of η^1-allyl–Fp complexes is the [3 + 2]-cycloaddition with electron-deficient alkenes [33]. The reaction proceeds via a non-concerted mechanism, to afford Fp-substituted cyclopentanes (Scheme 1.10).

Removal of the σ-substituted Fp group can be achieved by conversion into the cationic alkene–Fp complex using Ph_3CPF_6 and subsequent treatment with iodide, bromide or acetonitrile. Oxidative cleavage with ceric ammonium nitrate in methanol provides the methyl esters via carbon monoxide insertion followed by demetallation. The [3 + 2]-cycloaddition has been successfully applied to the synthesis of hydroazulenes (Scheme 1.11) [34]. This remarkable reaction takes advantage of the specific nucleophilic and electrophilic properties of η^1-allyl–, cationic η^5-dienyl–, cationic η^2-alkene– and η^4-diene–iron complexes, respectively.

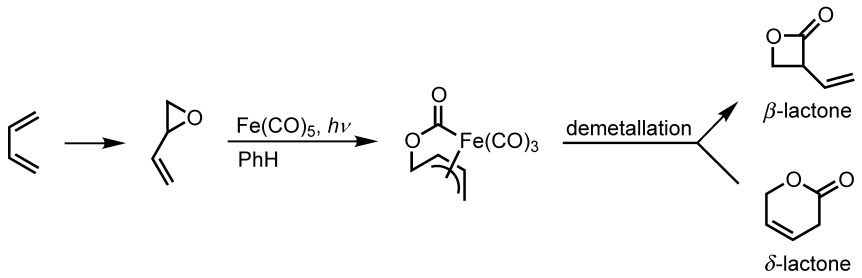


Acc = acceptor

Scheme 1.10



Scheme 1.11



Scheme 1.12

Cationic η^3-allyltetracarbonyliron complexes are generated by oxidative addition of allyl iodide to pentacarbonyliron followed by removal of the iodide ligand with $AgBF_4$ under a carbon monoxide atmosphere [35]. Similarly, photolysis of vinyl epoxides or cyclic vinyl sulfites with pentacarbonyliron or nonacarbonyldiiron provides π-allyltricarbonyliron lactone complexes. Oxidation with CAN provides by demetallation with concomitant coupling of the iron acyl carbon to one of the termini of the coordinated allyl moiety either β- or δ-lactones (Scheme 1.12) [36, 37]. In a related procedure, the corresponding π-allyltricarbonyliron lactam complexes lead to β- and δ-lactams [37].

In trimethylenemethane complexes, the metal stabilizes an unusual and highly reactive ligand which cannot be obtained in free form. Trimethylenemethanetricarbonyliron (R=H) was the first complex of this kind described in 1966 by Emerson and coworkers (Figure 1.2) [38]. It can be obtained by reaction of bromomethallyl alcohol with $Fe(CO)_5$. Trimethylenemethaneiron complexes have been applied for [3 + 2]-cycloaddition reactions with alkenes [39].

1.3.4
Acyl– and Carbene–Iron Complexes

Acyliron complexes have found many applications in organic synthesis [40]. Usually they are prepared by acylation of $[CpFe(CO)_2]^-$ with acyl chlorides or mixed anhydrides (Scheme 1.13). This procedure affords alkyl, aryl and α,β-unsaturated acyliron complexes. Alternatively, acyliron complexes can be obtained by treatment of $[Fe(C_5Me_5)(CO)_4]^+$ with organolithium reagents. α,β-Unsaturated acyliron complexes can be obtained by reaction of the same reagent with 2-alkyn-1-ols. Deprotonation of acyliron complexes with butyllithium generates the corresponding enolates, which can be functionalized by reaction with various electrophiles [40].

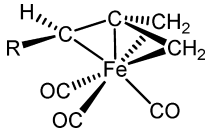
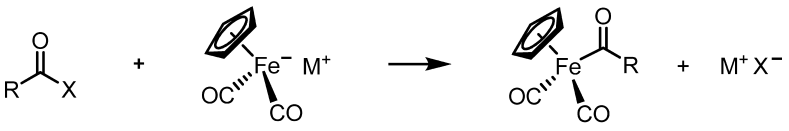
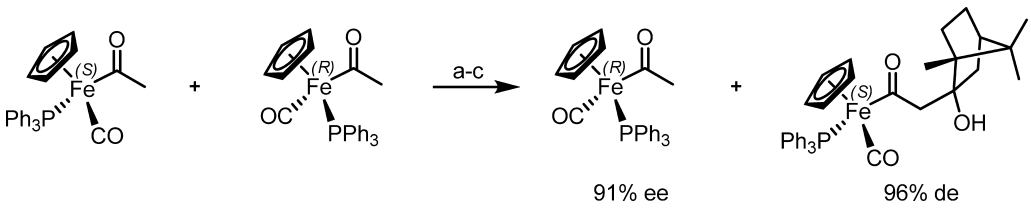


Figure 1.2 Trimethylenemethanetricarbonyliron complexes.



X = Cl, O(CO)OR'
M = Na, K

Scheme 1.13



a) BuLi, LiCl (1.5 eq.), THF, −78 °C; b) (1*R*)-(+)-camphor; c) MeOH

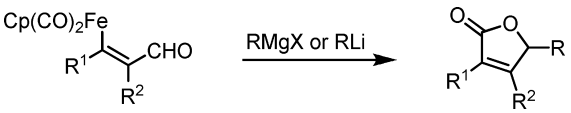
Scheme 1.14

Acyliron complexes with central chirality at the metal are obtained by substitution of a carbon monoxide with a phosphine ligand. Kinetic resolution of the racemic acyliron complex can be achieved by aldol reaction with (1*R*)-(+)-camphor (Scheme 1.14) [41]. Along with the enantiopure (R_{Fe})-acyliron complex, the (S_{Fe})-acyliron–camphor adduct is formed, which on treatment with base (NaH or NaOMe) is converted to the initial (S_{Fe})-acyliron complex. Enantiopure acyliron complexes represent excellent chiral auxiliaries, which by reaction of the acyliron enolates with electrophiles provide high asymmetric inductions due to the proximity of the chiral metal center. Finally, demetallation releases the enantiopure organic products.

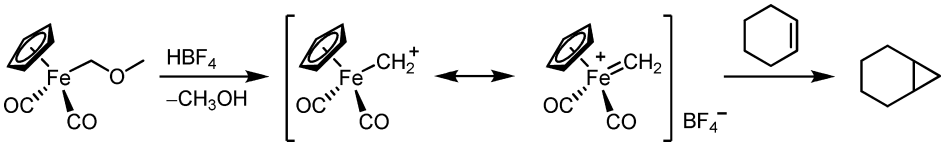
α,β-Unsaturated acyliron complexes are versatile reagents and show high stereoselectivity in many reactions, e.g. as dienophiles in Diels–Alder reactions [42], as Michael acceptors for heteronucleophiles [43] and in [3 + 2]-cycloadditions with allyltributylstannane to cyclopentanes [44].

Fp-substituted enones and enals undergo cyclocarbonylations on treatment with metal hydrides or metal alkyls to provide γ-lactones (Scheme 1.15) [45]. Similarly, electron-rich primary amines afford dihydropyrrolones with iron-substituted (*Z*)-enals in the presence of titanium tetrachloride and triethylamine [46].

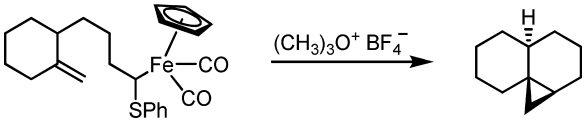
Dicarbonyl(η^5-cyclopentadienyl)iron–alkyl complexes represent useful precursors for iron–carbene complexes [47]. For example, iron–carbene complexes are intermediates in the acid-promoted reaction of Fp–alkyl ether derivatives with alkenes to provide cyclopropanes via a [2 + 1]-cycloaddition (Scheme 1.16).



Scheme 1.15



Scheme 1.16



Scheme 1.17

In a related strategy, Helquist and coworkers used thioether-substituted Fp complexes and applied the intermediate iron–carbene complexes to cyclopropanation (Scheme 1.17), C−H insertion and Si−H insertion reactions [48].

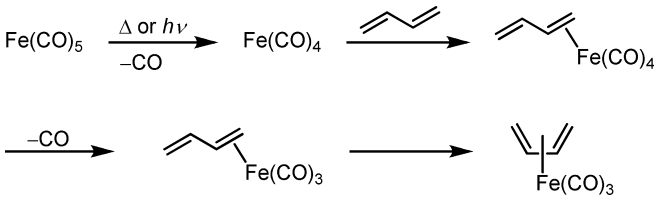
A cyclopentane annelation by intramolecular C−H insertion of intermediate cationic iron–carbene complexes has been applied to the synthesis of the fungal metabolite (±)-sterpurene [49].

1.3.5 Diene–Iron Complexes

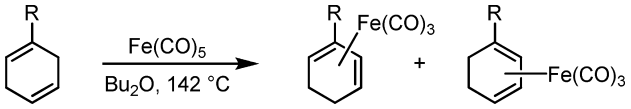
Acyclic and cyclic diene–iron complexes are stable compounds and have found a wide range of applications in organic synthesis [36, 50, 51]. The reactivity of the 1,3-diene system is altered drastically by coordination to the tricarbonyliron fragment. For example, the coordinated diene moiety does not undergo hydrogenation, hydroboration, dihydroxylation, Sharpless epoxidation, cyclopropanation and Diels–Alder cycloaddition reactions. Hence, the tricarbonyliron fragment has been used as a protecting group for diene systems. The reactivity of the diene unit towards electrophiles is decreased in the complex. However, the reactivity towards nucleophiles is increased due to donation of π-electrons to the metal. Therefore, the coordinated tricarbonyliron fragment may be regarded as an acceptor group. Moreover, the iron carbonyl fragment by its steric demand blocks one face of the diene moiety and serves as a stereo-directing group [51].

The classical protocol for synthesis of iron–diene complexes starts from the homoleptic pentacarbonyliron complex. In a stepwise fashion, via a dissociative mechanism, two carbonyl ligands are displaced by the diene system. However, thermal dissociation of the first CO ligand requires rather harsh conditions (ca. 140 °C). For acyclic 1,3-dienes, the diene ligand adopts an *s-cis* conformation to form stable η^4-complexes (Scheme 1.18).

Non-conjugated dienes isomerize during complexation to afford tricarbonyliron-coordinated conjugated dienes. This isomerization has been applied to a wide range of substituted cyclohexa-1,4-dienes available by Birch reduction from aromatic



Scheme 1.18



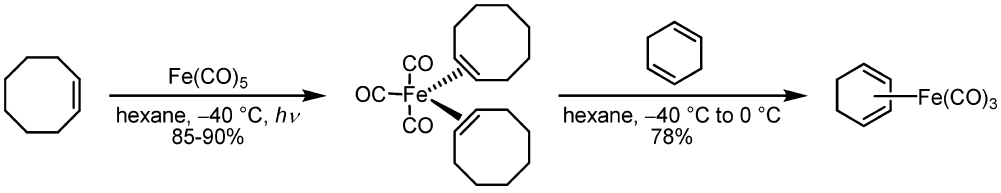
Scheme 1.19

compounds. However, often isomeric mixtures are formed by complexation of substituted cyclohexadienes (Scheme 1.19).

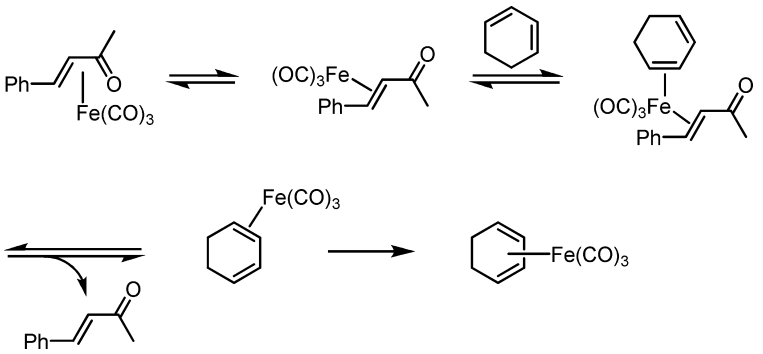
For introduction of the tricarbonyliron fragment under mild reaction conditions, tricarbonyliron transfer reagents have been developed [52]. Among them are tricarbonylbis(η^2-*cis*-cyclooctene)iron (Grevels' reagent) [53] and (η^4-benzylideneacetone) tricarbonyliron [54]. Grevels' reagent is prepared by photolytic reaction of pentacarbonyliron with *cis*-cyclooctene and transfers the tricarbonyliron fragment at temperatures below 0 °C (Scheme 1.20). Although the solid compound can be handled at room temperature, in solution the complex is very labile and stable only at temperatures below −35 °C.

(η^4-Benzylideneacetone)tricarbonyliron has been used for the synthesis of the tricarbonyliron complex of 8,8-diphenylheptafulvalene, which could not be prepared by reaction with pentacarbonyliron and dodecacarbonyltriiron owing to the sensitivity of the substrate to both heat and UV light. The mechanism which has been proposed for the transfer of the tricarbonyliron fragment using this reagent involves an initial η^4 to η^2 haptotropic migration (Scheme 1.21) [54b,c].

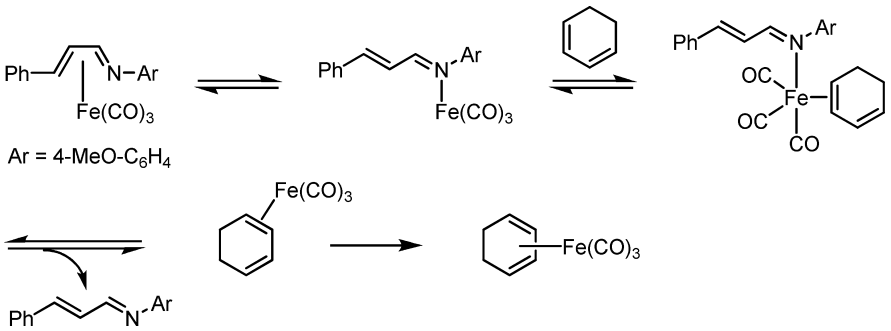
Because of the high lability of the reagents described above, (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes have been developed as alternative tricarbonyliron transfer reagents. They are best prepared by an ultrasound-promoted reaction of 1-azabuta-1,3-dienes with nonacarbonyldiiron in tetrahydrofuran at room temperature. Using (η^4-1-azabuta-1,3-diene)tricarbonyliron complexes the transfer of the tricarbonyliron unit proceeds in refluxing tetrahydrofuran in high yields [55a,b].



Scheme 1.20



Scheme 1.21

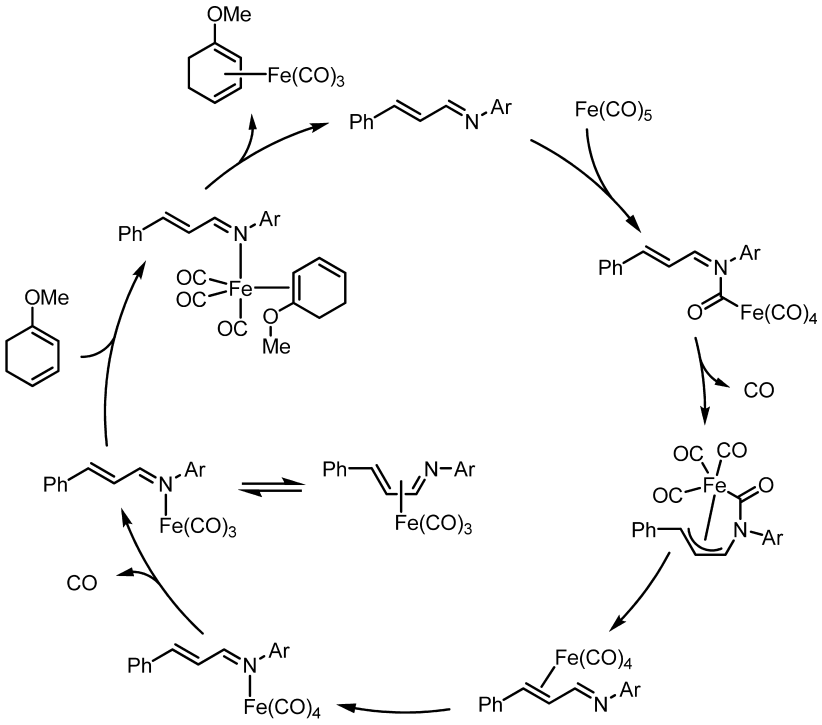


Scheme 1.22

Moreover, after transfer the free ligand can be recovered by crystallization. The mechanistic proposal for the transfer reaction is based on an initial η^4 to η^1 haptotropic migration (Scheme 1.22).

A catalytic process for the complexation of cyclohexadiene with pentacarbonyliron using 0.125 equivalents of the 1-azabuta-1,3-diene in refluxing dioxane affords quantitatively the corresponding tricarbonyliron complex [55c]. Supported by additional experimental evidence, the mechanism shown in Scheme 1.23 has been proposed for the 1-azadiene-catalyzed complexation [52].

1-Azabutadiene reacts with pentacarbonyliron by nucleophilic attack at a carbon monoxide ligand to form a σ-carbamoyliron complex. Subsequent intramolecular displacement of a carbon monoxide ligand affords an (η^3-allyl)carbamoyliron complex. Two consecutive haptotropic migrations (η^3 to η^2 and η^2 to η^1) provide a tetracarbonyl(η^1-imine)iron complex. Release of a second carbon monoxide generates tricarbonyl(η^1-imine)iron, a reactive 16-electron species. Via haptotropic migration (η^1 to η^4), this intermediate converts to the 18-electron (η^4-1-azabuta-1,3-diene) tricarbonyliron complex, the stoichiometric transfer reagent. At the stage of the reactive 16-electron intermediate, a double bond of the diene system can be coordinated at the metal. Regeneration of the 1-azadiene catalyst followed by haptotropic migration (η^2 to η^4) leads to the stable 18-electron complex,



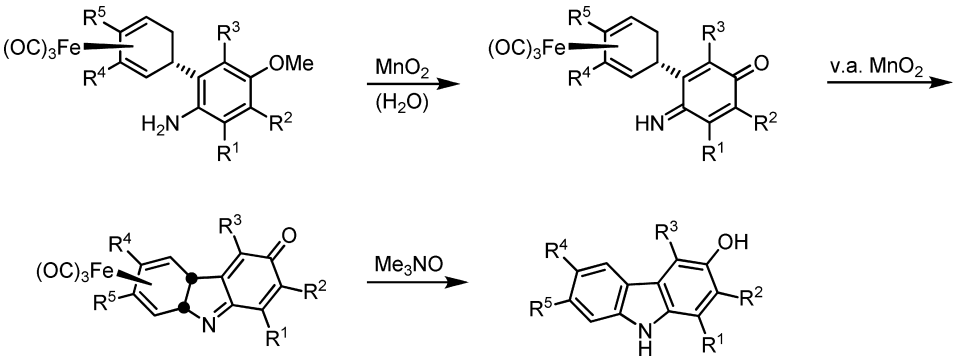
Scheme 1.23

tricarbonyliron(η^4-cyclohexa-1,3-diene)iron. This catalytic cycle contains metal complexes as substrate, product and catalytically active species.

The catalytic system described above has been further developed to an asymmetric catalytic complexation of prochiral 1,3-dienes (99% yield, up to 86% *ee*) using an optically active camphor-derived 1-azabutadiene ligand [56]. This method provides for the first time planar-chiral transition metal π-complexes by asymmetric catalysis.

Chemoselective oxidation of 4-methoxyanilines to quinonimines can be achieved in the presence of tricarbonyl(η^4-cyclohexadiene)iron complexes. This transformation has been used for the synthesis of carbazoles via intermediate tricarbonyliron-coordinated 4b,8a-dihydrocarbazol-3-one complexes (Scheme 1.24) [57].

The *p*-anisidine moiety is oxidized by commercial (water-containing) manganese dioxide to the non-cyclized quinonimine. Iron-mediated oxidative cyclization by treatment with *very active* manganese dioxide affords the tricarbonyliron-coordinated 4b,8a-dihydrocarbazol-3-one. The cyclohexadiene–iron complex is stable even in the presence of the adjacent quinonimine without any aromatization of both systems in an intramolecular redox reaction. The function of the tricarbonyliron fragment as protecting group becomes evident by demetallation with trimethylamine *N*-oxide leading to instantaneous aromatization of both rings. A number of 3-oxygenated carbazole alkaloids have been obtained by this route [58].

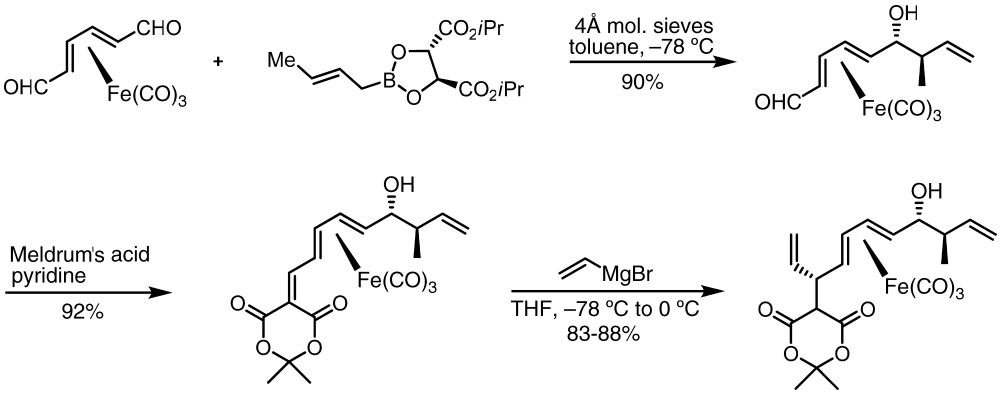


Scheme 1.24

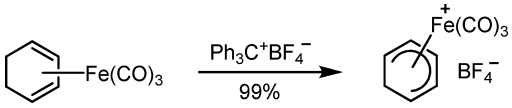
Kinetic resolution can be accomplished by addition of allyl boronates to aldehyde groups adjacent to the tricarbonyliron fragment [59]. For the synthesis of ikarugamycin, Roush and Wada developed an impressive asymmetric crotylboration of a prochiral *meso* complex using a chiral diisopropyl tartrate-derived crotylborane (Scheme 1.25) [60]. In the course of this synthesis, the stereo-directing effect of the tricarbonyliron fragment has been exploited twice to introduce stereospecifically a crotyl and a vinyl fragment.

Cyclohexadienylium–tricarbonyliron complexes are readily available by hydride abstraction from cyclohexadiene–tricarbonyliron complexes using triphenylcarbenium tetrafluoroborate [61]. They are stable and can be handled in air. The hydride ion is removed at one of the non-coordinated carbon atoms from the face opposite to the metal fragment. The resulting cyclohexadienylium system is stabilized as an η^5-ligand by the tricarbonyliron fragment (Scheme 1.26).

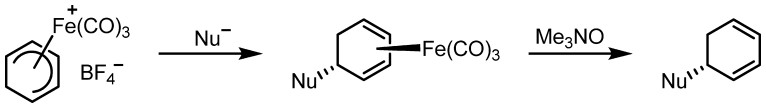
Cyclohexadienylium–tricarbonyliron complexes represent the most versatile iron complexes applied as building blocks in synthetic organic chemistry. Because of their positive charge, a large variety of nucleophiles undergo nucleophilic attack at the



Scheme 1.25



Scheme 1.26



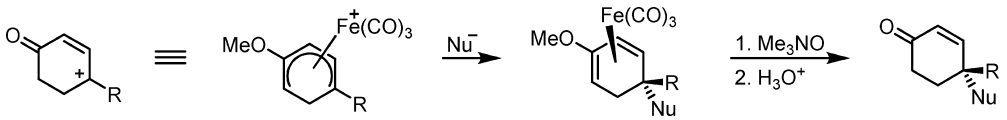
Scheme 1.27

coordinated ligand (Scheme 1.27). The attack of nucleophiles generally proceeds in high yields and takes place regioselectively at the terminus of the coordinated dienyl system (Davies–Green–Mingos rules) [62] and also stereoselectively *anti* to the tricarbonyliron fragment. Demetallation of the resulting functionalized cyclohexadienes to the corresponding free ligands can be achieved with different oxidizing agents (e.g. trimethylamine *N*-oxide).

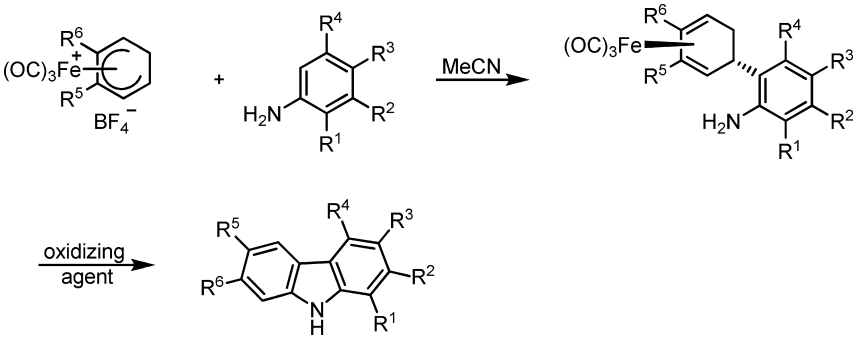
Additions to substituted dienyl systems, depending on the position of the substituents, their electronic properties and the steric demand of the nucleophile, may lead to a variety of regioisomeric products. However, in most cases the regiochemical outcome of the reaction can be predicted [63]. Addition of nucleophiles to tricarbonyliron-coordinated 1-alkyl-4-methoxy-substituted cyclohexadienyl cations permits the stereoselective construction of quaternary carbon centers (Scheme 1.28). The selectivity of this addition is governed by the regio-directing effect of the methoxy group, which directs the incoming nucleophile in the *para*-position, and the stereo-directing effect of the tricarbonyliron fragment (*anti* selectivity). These building blocks have been used for synthetic approaches to several natural products, e.g. (±)-limaspermine [64], the spirocyclic discorhabdin and prianosin alkaloids [65] and *O*-methyljoubertiamine [66].

Using cationic tricarbonyl(η^5-cyclohexadienyl)iron complexes as starting materials, different synthetic routes to a large number of carbazole alkaloids have been developed [51, 58, 67]. The first step is an electrophilic substitution of a substituted arylamine using the cyclohexadienyliron complex and provides the corresponding 5-aryl-substituted cyclohexadiene–iron complexes (Scheme 1.29).

The construction of the carbazole framework is completed by an iron-mediated oxidative cyclization which proceeds via an initial single electron transfer to generate a 17-electron radical cation intermediate. Iron-mediated oxidative



Scheme 1.28

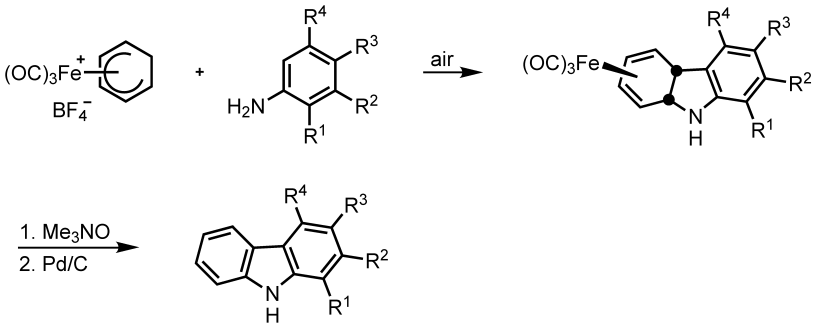


Scheme 1.29

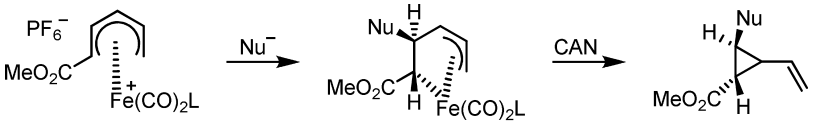
cyclization and subsequent aromatization can be accomplished in a one-pot procedure by using several oxidizing agents (e.g., *very active* manganese dioxide, iodine in pyridine, ferricenium hexafluorophosphate–sodium carbonate). This method has been applied to the total synthesis of a wide variety of carbazole alkaloids [67]. Alternatively, an iron-mediated oxidative cyclization in air leading to stable 4a,9a-dihydrocarbazole–iron complexes has been developed. Final demetallation and dehydrogenation of these complexes afford the carbazoles (Scheme 1.30) [67, 68].

A further route, via initial oxidation of the arylamine to a quinonimine followed by oxidative cyclization to an iron-coordinated 4b,8a-dihydrocarbazol-3-one and demetallation to a 3-hydroxycarbazole, has been described above (Scheme 1.24).

Acyclic pentadienyliron complexes show a similar reactivity towards nucleophiles but have found less application so far. Donaldson and coworkers reported an interesting cyclopropanation starting from a pentadienyliron complex (Scheme 1.31) [69]. This procedure has been used for the stereoselective synthesis of cyclopropylglycines [70], the preparation of the C_9-C_{16} alkenylcyclopropane segment of ambruticin [71] and the synthesis of hydrazulenes via divinylcyclopropanes [72].



Scheme 1.30



L = CO, PPh_3

Scheme 1.31

1.3.6 Ferrocenes

Ferrocene is an iron(II) sandwich complex with two cyclopentadienyl ligands (Figure 1.3). Since its discovery in 1951 [4], ferrocene has been the subject of extensive investigations due to its reactivity, structural features and potential for applications [73].

Ferrocene is air-stable, can be sublimed without decomposition and reacts with electrophiles by substitution at the cyclopentadienyl ring. The mechanism differs from classical electrophilic aromatic substitution in the way that the electrophile first attacks at the metal center and is subsequently transferred to the ligand followed by deprotonation. Oxidation of ferrocene gives the blue ferricenium ion $[Fe(C_5H_5)_2]^+$, which is used as an oxidizing agent. Ferrocenes which are homoannular disubstituted with two different substituents are planar chiral. This feature has been widely exploited for applications in various asymmetric catalytic reactions. Especially ferrocenylphosphanes represent useful chiral ligands [74]. Also planar chiral ferrocenes with additional chiral substituents have been applied in asymmetric catalysis, and even a combination of planar, central and axial chirality was employed (Figure 1.4). An example of asymmetric synthesis using chiral ferrocene ligands is described below (Section 1.4.2).

1.3.7 Arene–Iron Complexes

Two types of arene–iron complexes are known in the literature, monocationic arene–FeCp and dicationic bis(arene)Fe complexes [75]. The former type is more stable and shows a more useful chemistry. Arene–FeCp complexes can be prepared

Figure 1.3 Ferrocene.

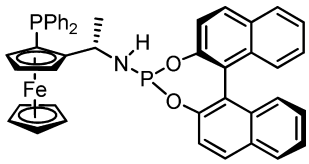
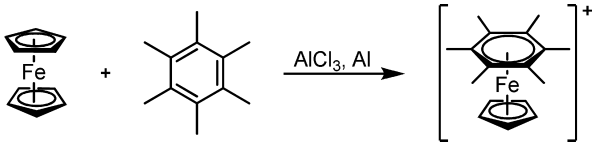


Figure 1.4 A ferrocene with planar, central and axial chirality.



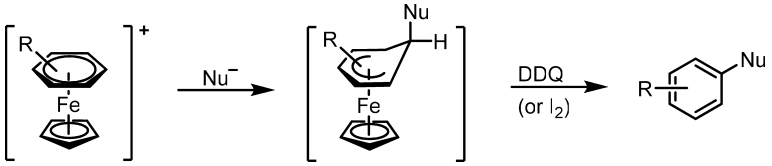
Scheme 1.32

by ligand exchange from ferrocene with the corresponding aromatic compound in the presence of aluminum trichloride and aluminum powder (Scheme 1.32).

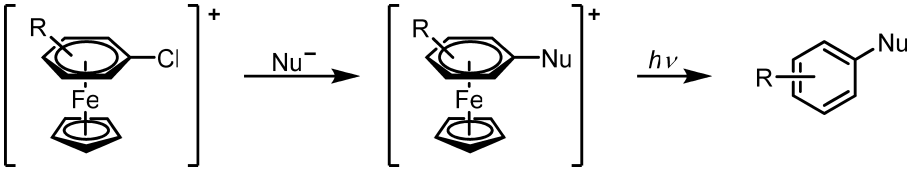
The metal reduces the electron density at the arene ligand, thus making it more susceptible to nucleophilic attack (Scheme 1.33). Arene–FeCp complexes react with a great variety of nucleophiles following the Davies–Green–Mingos rules [62] preferentially at the arene ring and stereoselectively *anti* to the metal. Alkyllithium compounds add readily at the arene ligand. Only in the case of steric hindrance addition at the Cp ligand is observed.

Electron-donating substituents direct the incoming nucleophile predominantly to the *meta*-position and electron-withdrawing substituents to the *ortho*-position. Oxidative demetallation (DDQ, iodine) is applied to reoxidize the cyclohexadienyl ligand, releasing a substituted arene. Addition of nucleophiles to halobenzene–FeCp complexes leads to nucleophilic substitution of the halo substituent (Scheme 1.34). Demetallation of the product complexes is achieved by irradiation with sunlight or UV light in acetone or acetonitrile.

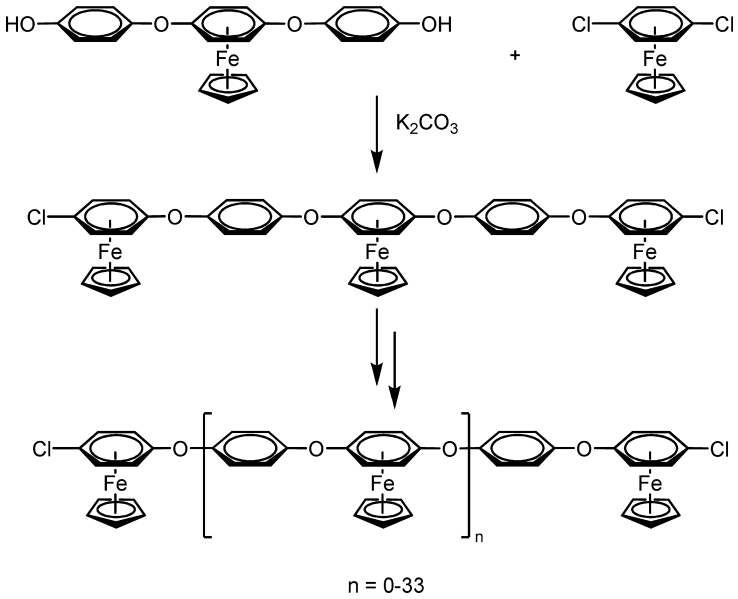
This reaction is a powerful tool and represents an alternative for the synthesis of substituted arenes difficult to prepare via classical electrophilic or nucleophilic aromatic substitution. Using bi- or polyfunctional arenes as starting materials, this reaction affords novel organoiron polymers [76] (Scheme 1.35).



Scheme 1.33



Scheme 1.34



Scheme 1.35

Dicationic bis(arene)iron complexes are prepared from Fe(II) salts using the corresponding arene as solvent in the presence of aluminum trichloride at elevated temperatures. Because of the double positive charge, they easily add two nucleophiles at one arene ring.

1.4
Catalysis Using Iron Complexes

The difficulty in removing metal residues from the product induced the search for iron-catalyzed reactions [77]. However, iron complexes can play different roles in catalytic processes:

1. as substrate and/or product;
2. as ligands for other transition metal catalysts to achieve activation and stereocontrol;
3. as catalytically active species.

1.4.1
Iron Complexes as Substrates and/or Products in Catalytic Reactions

The first aspect is illustrated by the synthesis of tricarbonyl(η^4-1,3-diene)iron complexes from pentacarbonyliron in the presence of catalytic amounts of a 1-azabuta-

diene which forms *in situ* during the catalytic cycle a tricarbonyliron transfer reagent (Scheme 1.23) [52]. The 1-azabutadiene represents the catalytically active species in this process. Electrocatalysis with ferrocenes also belongs to this category [78, 79].

1.4.2
Iron Complexes as Ligands for Other Transition Metal Catalysts

Organoiron complexes have been applied as ligands for processes catalyzed by other transition metals in order to activate them or to achieve stereocontrol. This principle has been utilized by readily available ferrocenes bearing additional coordinating groups at their cyclopentadienyl rings [74]. Due to their planar chirality, substituted ferrocenes, often in combination with additional central chirality of pendant groups, have been extensively investigated as ligands for asymmetric catalysis. A few examples of commercially available ferrocene ligands are shown in Figure 1.5.

A broad variety of asymmetric reactions has been studied using chiral ferrocene ligands, e.g. asymmetric hydrogenation, asymmetric metal-catalyzed coupling reactions and enantioselective nucleophilic additions to aldehydes and imines. An example of such a catalytic process is the synthesis of the peroxime proliferator activated receptor (PPAR) agonist, applying a rhodium-catalyzed hydrogenation of a cinnamic acid derivative in 78% yield and 92% *ee* (Scheme 1.36) [80]. In this particular case, the ferrocene ligand Walphos proved to be most efficient.

1.4.3
Iron Complexes as Catalytically Active Species

This section provides only a brief insight into iron-catalyzed reactions. Iron complexes as catalytically active species undergo typical steps of transition metal catalysis

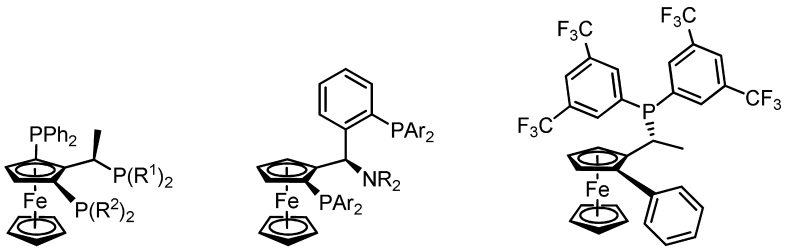
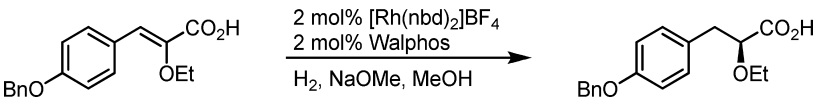
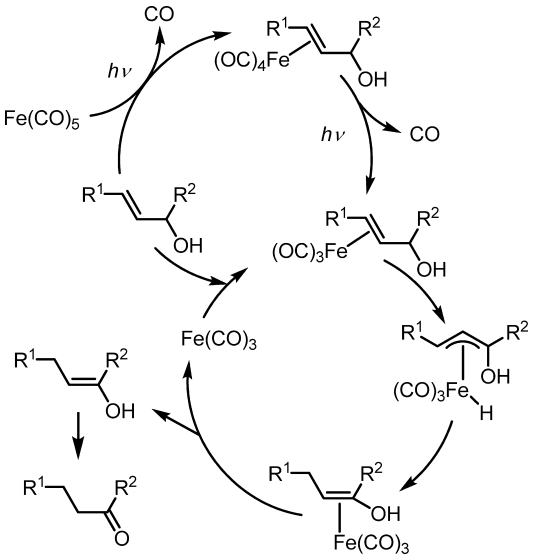


Figure 1.5 Commercially available chiral ferrocene ligands.



Scheme 1.36



Scheme 1.37

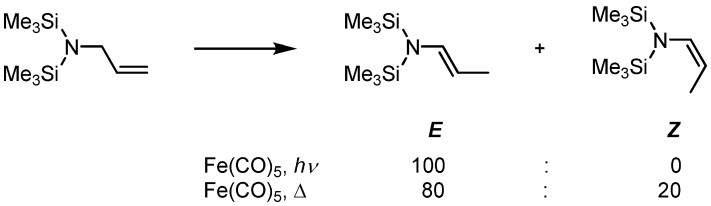
such as oxidative addition and reductive elimination, thus leading to a reversible change of the formal oxidation state of the metal.

Pentacarbonyliron can catalyze the isomerization of double bonds under photochemical conditions. Using catalyst loadings as low as 1–5 mol%, this process proceeds smoothly for allyl alcohols, which isomerize to the corresponding saturated carbonyl compounds.

The mechanism of the catalytic cycle is outlined in Scheme 1.37 [11]. It involves the formation of a reactive 16-electron tricarbonyliron species by coordination of allyl alcohol to pentacarbonyliron and sequential loss of two carbon monoxide ligands. Oxidative addition to a π-allyl hydride complex with iron in the oxidation state +2, followed by reductive elimination, affords an alkene–tricarbonyliron complex. As a result of the [1, 3]-hydride shift the allyl alcohol has been converted to an enol, which is released and the catalytically active tricarbonyliron species is regenerated. This example demonstrates that oxidation and reduction steps can be merged to a one-pot procedure by transferring them into oxidative addition and reductive elimination using the transition metal as a reversible switch. Recently, this reaction has been integrated into a tandem isomerization-aldolization reaction which was applied to the synthesis of indanones and indenones [81] and for the transformation of vinylic furanoses into cyclopentenones [82].

In a similar reaction, allylamines can be isomerized to afford enamines. Photochemical isomerization of the silylated allylamine in the presence of catalytic amounts of pentacarbonyliron provided exclusively the *E*-isomer of the enamine, whereas a thermally induced double bond shift provided a 4:1 mixture of the *E*- and *Z*-enamines (Scheme 1.38) [13].

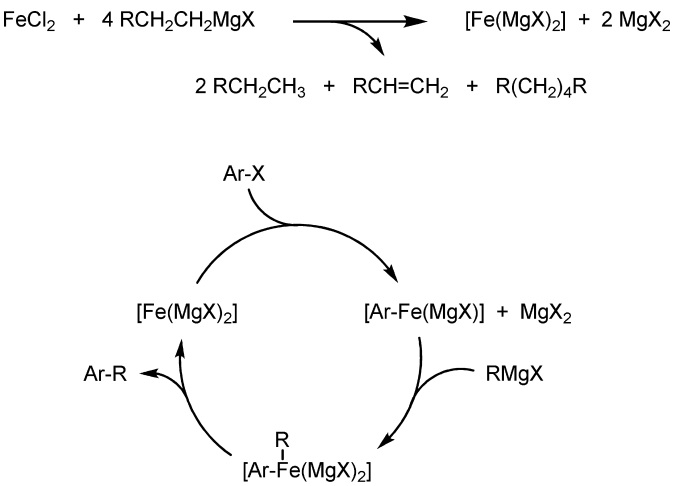
Pentacarbonyliron has also been applied as catalyst for the reduction of nitroarenes by carbon monoxide and water to afford anilines [17, 83].



Scheme 1.38

A comparison of the electronic configuration of iron with that of nickel suggests that iron systems which are isoelectronic to the redox couple Ni(0)/Ni(II) could have potential as catalysts. This would apply to the Fe(–II)/Fe(0) system. The increased nucleophilicity of the Fe(–II) species should facilitate oxidative addition reactions, which often represent the limiting step. In fact, several iron-catalyzed cross-coupling reactions of Grignard or organomanganese reagents with alkenyl halides or aryl chlorides, tosylates and triflates have been reported recently [84, 85]. In these examples, the Fe(–II)/Fe(0) redox system appears to drive the catalytic cycle. A mechanism involving a catalytically active Fe(–II) species has been postulated by Fürstner *et al.* for this cross-coupling reaction (Scheme 1.39) [77, 86].

The "inorganic Grignard" species $[Fe(MgX)_2]$, which has not yet been structurally confirmed, is regarded as the propagating agent. Oxidative addition of an aryl halide generates an Fe(0) complex, which is alkylated by another Grignard reagent. Reductive elimination provides the organic product and regenerates the catalytically active species. The Fe(–II)/Fe(0) redox-couple appears to have great potential for further applications in organic synthesis.



Scheme 1.39

References

1 (a) A. J. Pearson, *Metallo-organic Chemistry*, Wiley, Chichester, 1985; (b) J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Application of Organotransition Metal Chemisty*, University Science Books, Mill Valley, CA, 1987; (c) S. G. Davies, *Organotransition Metal Chemistry: Application to Organic Synthesis*, Pergamon Press, Oxford, 1989; (d) L. S. Hegedus, *Transition Metals in the Synthesis of Complex Organic Molecules*, 2nd edn., University Science Books, Sausalito, CA, 1999; (e) J. Tsuji, Transition Metal Reagents and Catalysts, *Innovations in Organic Synthesis*, Wiley, Chichester, 2000.

2 L. Mond, F. Quinke, *J. Chem. Soc.* 1891, **59**, 604.

3 M. Berthelot, *C. R. Hebd. Seances Acad. Sci.* 1891, **112**, 1343.

4 T. J. Kealy, P. L. Pauson, *Nature* 1951, **168**, 1039.

5 W. Reppe, H. Vetter, *Justus Liebigs Ann. Chem.* 1953, **582**, 133.

6 (a) M. Tamura, J. Kochi, *Synthesis* 1971, 303; (b) M. Tamura, J. Kochi, *J. Am. Chem. Soc.* 1971, **93**, 1487.

7 A. J. Pearson, *Iron Compounds in Organic Synthesis*, Academic Press, London, 1994.

8 H.-J. Knölker, H. Goesmann, R. Klauss, *Angew. Chem.* 1999, **111**, 727; *Angew. Chem. Int. Ed.* 1999, **38**, 702.

9 H.-J. Knölker, E. Baum, H. Goesmann, R. Klauss, *Angew. Chem.* 1999, **111**, 2196. *Angew. Chem. Int. Ed.* 1999, **38**, 2064.

10 E. J. Corey, G. Moinet, *J. Am. Chem. Soc.* 1973, **95**, 7185.

11 (a) H. Cherkaoui, M. Soufiaoui, R. Grée, *Tetrahedron* 2001, **57**, 2379; (b) R. Uma, C. Crevisy, R. Grée, *Chem. Rev.* 2003, **103**, 27.

12 R. J. P. Corriu, V. Huynh, J. J. E. Moreau, M. Pataud-Sat, *J. Organomet. Chem.* 1983, **255**, 359.

13 K. Paulini, H.-U. Reissig, *Liebigs Ann. Chem.* 1991, 455.

14 R. Noyori, *Acc. Chem. Res.* 1979, **12**, 61.

15 A. A. O. Sarhan, *Curr. Org. Chem.* 2001, **5**, 827.

16 (a) R. Noyori, S. Makino, T. Okita, Y. Hayakawa, *J. Org. Chem.* 1975, **40**, 806; (b) H. Takaya, Y. Hayakawa, S. Makino, R. Noyori, *J. Am. Chem. Soc.* 1978, **100**, 1778.

17 J. M. Landesberg, L. Katz, C. Olsen, *J. Org. Chem.* 1972, **37**, 930.

18 M. Ryang, I. Rhee, S. Tsutsumi, *Bull. Chem. Soc. Jpn.* 1964, **37**, 341.

19 (a) J. P. Collman, *Acc. Chem. Res.* 1975, **8**, 342; (b) M. P. Cooke, Jr., R. M. Parlman, *J. Am. Chem. Soc.* 1975, **97**, 6863.

20 M. Periasamy, C. Rameshkumar, U. Radhakrishnan, A. Devasagayaraj, *Curr. Sci.* 2000, **78**, 1307.

21 (a) E. Weiss, W. Hübel, *J. Inorg. Nucl. Chem.* 1959, **11**, 42; (b) E. Weiss, R. Merenyi, W. Hübel, *Chem. Ind. (London)* 1960, 407; (c) E. Weiss, R. Merenyi, W. Hübel, *Chem. Ber.* 1962, **95**, 1170.

22 (a) H.-J. Knölker, J. Heber, C. H. Mahler, *Synlett* 1992, 1002; (b) H.-J. Knölker, J. Heber, *Synlett* 1993, 924; (c) H.-J. Knölker, E. Baum, J. Heber, *Tetrahedron Lett.* 1995, **36**, 7647.

23 (a) A. J. Pearson, R. J. Shively, Jr., R. A. Dubbert, *Organometallics* 1992, **11**, 4096; (b) A. J. Pearson, R. J. Shively, Jr., *Organometallics* 1994, **13**, 578; (c) A. J. Pearson, X. Yao, *Synlett* 1997, 1281.

24 H.-J. Knölker, A. Braier, D. J. Bröcher, P. G. Jones, H. Piotrowski, *Tetrahedron Lett.* 1999, **40**, 8075.

25 H.-J. Knölker, S. Cämmerer, *Tetrahedron Lett.* 2000, **41**, 5035.

26 (a) P. L. Pauson, *Tetrahedron* 1985, **41**, 5855; (b) J. Blanco-Urgoiti, L. Añorbe, L. Pérez-Serrano, G. Domínguez, J. Pérez-Castells, *Chem. Soc. Rev.* 2004, **33**, 32.

27 A. J. Pearson, R. A. Dubbert, *J. Chem. Soc., Chem. Commun.* 1991, 202.

28 C. Rameshkumar, M. Periasamy, *Tetrahedron Lett.* 2000, **41**, 2719.

29 M. Periasamy, C. Rameshkumar, A. Mukkanti, *J. Organomet. Chem.* 2002, **649**, 209.

30 (a) B. W. Roberts, J. Wong, *J. Chem. Soc., Chem. Commun.* 1977, 20; (b) B. W. Roberts, M. Ross, J. Wong, *J. Chem. Soc., Chem. Commun.* 1980, 428.

31 M. Rosenblum, A. Bucheister, T. C. T. Chang, M. Cohen, M. Marsi, S. B. Samuels, D. Scheck, N. Sofen, J. C. Watkins, *Pure Appl. Chem.* 1984, **56**, 129.

32 (a) J. Benaim, A. L'Honore, *J. Organomet. Chem.* 1980, **202**, C53; (b) D. J. Bates, M. Rosenblum, S. B. Samuels, *J. Organomet. Chem.* 1981, **209**, C55.

33 M. Rosenblum, *Acc. Chem. Res.* 1974, **7**, 122.

34 N. Grenco, D. Marten, S. Raghu, M. Rosenblum, *J. Am. Chem. Soc.* 1976, **98**, 848.

35 H. D. Murdoch, E. Weiss, *Helv. Chim. Acta* 1962, **45**, 1927.

36 L. R. Cox, S. V. Ley, *Chem. Soc. Rev.* 1998, **27**, 301.

37 S. V. Ley, L. R. Cox, G. Meek, *Chem. Rev.* 1996, **96**, 423.

38 (a) G. F. Emerson, K. Ehrlich, W. P. Giering, P. C. Lauterbur, *J. Am. Chem. Soc.* 1966, **88**, 3172; (b) K. Ehrlich, G. Emerson, *J. Am. Chem. Soc.* 1972, **94**, 2464.

39 M. Franck-Neumann, A. Kastler, *Synlett* 1995, 61.

40 For reviews, see: (a) K. Rück-Braun, M. Mikulas, P. Amrhein, *Synthesis* 1999, 727; (b) K. Rück-Braun, in *Transition Metals for Organic Synthesis – Building Blocks and Fine Chemicals*, Vol. 1, ed. M. Beller, C. Bolm, Wiley-VCH, Weinheim, 1998, Chap. 3.12, p. 523;(c) K. Rück-Braun, in *Transition Metals for Organic Synthesis – Building Blocks and Fine Chemicals*, Vol.1, 2nd edn., ed. M. Beller, C. Bolm, Wiley-VCH, Weinheim, 2004, Chap. 3.10, p. 575.

41 S. C. Case-Green, J. F. Costello, S. G. Davies, N. Heaton, C. J. R. Hedgecock, V. M. Humphreys, M. R. Metzler, J. C. Prime, *J. Chem. Soc., Perkin Trans. 1* 1994, 933.

42 (a) J. W. Herndon, *J. Org. Chem.* 1986, **51**, 2853; (b) K. Rück-Braun, J. Kühn, D. Scholl-Meyer, *Chem. Ber.* 1996, **129**, 1057.

43 S. G. Davies, N. M. Garrido, P. A. McGee, J. P. Shilvock, *J. Chem. Soc., Perkin Trans. 1* 1999, 3105.

44 (a) J. W. Herndon, *J. Am. Chem. Soc.* 1987, **109**, 3165; (b) J. W. Herndon, C. Wu, *Synlett* 1990, 411; (c) J. W. Herndon, C. Wu, J. J. Harp, *Organometallics* 1990, **9**, 3157.

45 C. Möller, M. Mikulas, F. Wierchem, K. Rück-Braun, *Synlett* 2000, 182.

46 K. Rück-Braun, T. Martin, M. Mikulas, *Chem. Eur. J.* 1999, **5**, 1028.

47 (a) M. Brookhart, W. B. Studabaker, *Chem. Rev.* 1987, **87**, 411; (b) P. Helquist, in *Advances in Metal–Organic Chemistry*, Vol. 2, ed. L. S. Liebeskind, JAI Press, London, 1991, p. 143; (c) W. Petz, *Iron–Carbene Complexes*, Springer, Berlin, 1993.

48 E. J. O'Connor, S. Brandt, P. Helquist, *J. Am. Chem. Soc.* 1987, **109**, 3739.

49 (a) S.-K. Zhao, P. Helquist, *J. Org. Chem.* 1990, **55**, 5820; (b) S. Ishii, S. Zhao, G. Mehta, C. J. Knors, P. Helquist, *J. Org. Chem.* 2001, **66**, 3449.

50 (a) A. J. Pearson, *Acc. Chem. Res.* 1980, **13**, 463; (b) R. Grée, *Synthesis* 1989, 341; (c) A. J. Pearson, in *Comprehensive Organic Synthesis*, Vol. 4, ed. B. M. Trost, Pergamon Press, Oxford, 1991, Chap. 3.4, p. 663; (d) W. A. Donaldson, *Aldrichim. Acta* 1997, **30**, 17. (e) W. A. Donaldson, *Curr. Org. Chem.* 2000, **4**, 837; (f) W. A. Donaldson, in *The Chemistry of Dienes and Polyenes*, Vol. 2, ed. Z. Rappoport, Wiley, Chichester, 2000, Chap. 11, p. 885.

51 (a) H.-J. Knölker, *Synlett* 1992, 371; (b) H.-J. Knölker, in *Transition Metals for Organic Synthesis – Building Blocks and Fine Chemicals*, Vol. 1, ed. M. Beller, C. Bolm, Wiley-VCH, Weinheim, 1998, Chap. 3.13, p. 534; (c) H.-J. Knölker, *Chem. Soc. Rev.* 1999, **28**, 151; (d) H.-J. Knölker, A. Braier, D. J. Bröcher, S. Cämmerer, W. Fröhner, P. Gonser, H. Hermann, D. Herzberg, K. R. Reddy, G. Rohde, *Pure Appl. Chem.* 2001, **73**, 1075; (e) H.-J. Knölker, in *Transition Metals for Organic Synthesis – Building Blocks and Fine Chemicals*, Vol. 1, 2nd edn., ed. M. Beller, C. Bolm, Wiley-VCH, Weinheim, 2004, Chap. 3.11, p. 585.

52 H.-J. Knölker, *Chem. Rev.* 2000, **100**, 2941.

53 H. Fleckner, F.-W. Grevels, D. Hess, *J. Am. Chem. Soc.* 1984, **106**, 2027.

54 (a) J. A. S Howell, B. F. G Johnson, P. L. Josty, J. Lewis, *J. Organomet. Chem.* 1972, **39**, 329; (b) C. R. Graham, G. Scholes, M. Brookhart, *J. Am. Chem. Soc.* 1977, **99**, 1180; (c) M. Brookhart, G. O. Nelson, *J. Organomet. Chem.* 1979, **164**, 193.

55 (a) H.-J. Knölker, G. Baum, N. Foitzik, H. Goesmann, P. Gonser, P. G. Jones, H. Röttele, *Eur. J. Inorg. Chem.* 1998, 993; (b) H.-J. Knölker, B. Ahrens, P. Gonser, M. Heininger, P. G. Jones, *Tetrahedron* 2000, **56**, 2259; (c) H.-J. Knölker, E. Baum, P. Gonser, G. Rohde, H. Röttele, *Organometallics* 1998, **17**, 3916.

56 (a) H.-J. Knölker, H. Herrmann, *Angew. Chem.* 1996, **108**, 363; *Angew. Chem., Int. Ed. Engl.* 1996, **35**, 341; (b) H.-J. Knölker, H. Goesmann, H. Hermann, D. Herzberg, G. Rohde, *Synlett* 1999, 421; (c) H.-J. Knölker, H. Hermann, D. Herzberg, *Chem. Commun.* 1999, 831.

57 H.-J. Knölker, M. Bauermeister, J.-B. Pannek, M. Wolpert, *Synthesis* 1995, 397.

58 (a) H.-J. Knölker, G. Schlechtingen, *J. Chem. Soc., Perkin Trans. 1* 1997, 349; (b) H.-J. Knölker, E. Baum, T. Hopfmann, *Tetrahedron* 1999, **55**, 10391; (c) H.-J. Knölker, T. Hopfmann, *Tetrahedron* 2002, **58**, 8937.

59 W. R. Roush, J. C. Park, *Tetrahedron Lett.* 1990, **31**, 4707.

60 W. R. Roush, C. K. Wada, *J. Am. Chem. Soc.* 1994, **116**, 2151.

61 E. O. Fischer, R. D. Fischer, *Angew. Chem.* 1960, **72**, 919.

62 S. G. Davies, M. L. H. Green, D. M. P. Mingos, *Tetrahedron* 1978, **34**, 3047.

63 W. A. Donaldson, L. Shang, C. Tao, Y. K. Yun, M. Ramaswamy, V. G. Young, Jr., *J. Organomet. Chem.* 1997, **539**, 87.

64 (a) A. J. Pearson, D. C. Rees, *J. Am. Chem. Soc.* 1982, **104**, 1118; (b) A. J. Pearson, D. C. Rees, *J. Chem. Soc., Perkin Trans 1* 1982, 2467.

65 (a) H.-J. Knölker, R. Boese, K. Hartmann, *Angew. Chem.* 1989, **101**, 1745; *Angew. Chem. Int. Ed. Engl.* 1989, **28**, 1678. (b) H.-J. Knölker, K. Hartmann, *Synlett* 1991, 428.

66 (a) A. J. Pearson, I. C. Richards, D. V. Gardner, *J. Org. Chem.* 1984, **49**, 3887; (b) G. R. Stephenson, D. A. Owen, H. Finch, S. Swanson, *Tetrahedron Lett.* 1991, **32**, 1291.

67 (a) H.-J. Knölker, K. R. Reddy, *Chem. Rev.* 2002, **102**, 4303; (b) H.-J. Knölker, *Top. Curr. Chem.* 2005, **244**, 115; (c) H.-J. Knölker, K. R. Kethiri, in *The Alkaloids*, Vol. 65, ed. G. A. Cordell, Academic Press, Amsterdam, 2008, p. 1.

68 (a) H.-J. Knölker, W. Fröhner, *Tetrahedron Lett.* 1999, **40**, 6915; (b) H.-J. Knölker, E. Baum, K. R. Reddy, *Chirality* 2000, **12**, 526; (c) H.-J. Knölker, M. Wolpert, *Tetrahedron* 2003, **59**, 5317; (d) R. Czerwonka, K. R. Reddy, E. Baum, H.-J. Knölker, *Chem. Commun.* 2006, 711.

69 (a) Y. K. Yun, W. A. Donaldson, *J. Am. Chem. Soc.* 1997, **119**, 4084. (b) Y. K. Yun, K. Godula, Y. Cao, W. A. Donaldson, *J. Org. Chem.* 2003, **68**, 901.

70 (a) K. Godula, W. A. Donaldson, *Tetrahedron Lett.* 2001, **42**, 153; (b) N. J. Wallock, W. A. Donaldson, *Tetrahedron Lett.* 2002, **43**, 4541.

71 J. M. Lukesh, W. A. Donaldson, *Chem. Commun.* 2005, 110.

72 N. J. Wallock, D. W. Bennett, T. Siddiquee, D. T. Haworth, W. A. Donaldson, *Synthesis* 2006, 3639.

73 A. Togni, T. Hayashi, *Ferrocenes*, VCH, Weinheim, 1995.

74 (a) L.-X. Dai, T. Tu, S.-L. You, W.-P. Deng, X.-L. Hou, *Acc. Chem. Res.* 2003, **36**, 659; (b) R. Gomez Arrayas, J. Adrio, J. C. Carretero, *Angew. Chem.* 2006, **118**, 7836. *Angew. Chem. Int. Ed.* 2006, **45**, 7674.

75 (a) D. Astruc, *Tetrahedron* 1983, **39**, 4027; (b) A. S. Abd-El-Aziz, S. Bernardin, *Coord. Chem. Rev.* 2000, **203**, 219.

76 A. S. Abd-El-Aziz, E. K. Todd, *Coord. Chem. Rev.* 2003, **246**, 3.

77 C. Bolm, J. Legros, J. Le Paih, L. Zani, *Chem. Rev.* 2004, **104**, 6217.
78 D. Astruc, *Angew. Chem.* 1988, **100**, 662; *Angew. Chem. Int. Ed. Engl.* 1988, **27**, 643.
79 E. Steckhan, *Top. Curr. Chem.* 1997, **185**.
80 I. N. Houpis, L. E. Patterson, C. A. Alt, J. R. Rizzo, T. Y. Zhang, M. Haurez, *Org. Lett.* 2005, **7**, 1947.
81 J. Petrignet, T. Roisnel, R. Grée, *Chem. Eur. J.* 2007, **13**, 7374.
82 J. Petrignet, I. Prathap, S. Chandrasekhar, J. S. Yadav, R. Grée, *Angew. Chem.* 2007, **119**, 6413; *Angew. Chem. Int. Ed.* 2007, **46**, 6297.
83 K. Cann, T. Cole, W. Slegeir, R. Pettit, *J. Am. Chem. Soc.* 1978, **100**, 3969.
84 A. Fürstner, R. Martin, *Chem. Lett.* 2005, **34**, 624.
85 G. Cahiez, V. Habiak, C. Duplais, A. Moyeux, *Angew. Chem.* 2007, **119**, 4442; *Angew. Chem. Int. Ed.* 2007, **46**, 4364.
86 A. Fürstner, A. Leitner, M. Mendez, H. Krause, *J. Am. Chem. Soc.* 2002, **124**, 13856.