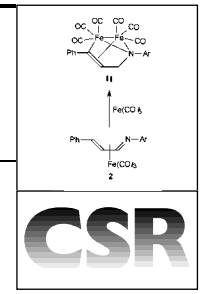
Transition metal complexes in organic synthesis. Part 47.[1] Organic synthesis *via* tricarbonyl(η⁴-diene)iron complexes



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The protection of conjugated dienes by coordination to the tricarbonyliron fragment offers many potential applications of the resulting complexes to organic synthesis. The preparation of tricarbonyl(η⁴-1,3-diene)iron complexes is readily achieved by a 1-azabutadiene-catalyzed complexation of the free ligands. An asymmetric catalytic complexation of prochiral cyclohexa-1,3-dienes with pentacarbonyliron using chiral 1-azabutadienes affords chiral nonracemic complexes. The chiral tricarbonyliron complexes of acyclic butadienes represent versatile starting materials for the synthesis of a broad range of polyunsaturated natural products. Consecutive carbon–carbon and carbon–nitrogen bond formations of the tricarbonyliron–cyclohexa-1,3-diene complexes and arylamines provide many biologically active carbazole alkaloids and a tetracyclic subunit of the discorhabdin alkaloids. The iron-mediated [2+2+1] cycloaddition of trimethylsilylacetylenes and carbon monoxide affords stable 2,5-bis(trimethylsilyl)-substituted cyclopentadienones which are useful substrates for further cycloadditions.

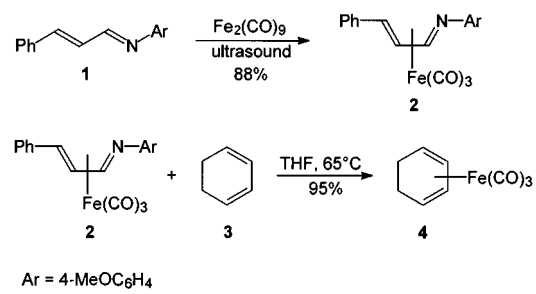
1 Introduction

Tricarbonyl(η⁴-1,3-diene)iron complexes represent important intermediates and offer versatile applications for organic synthesis.[2] The tricarbonyliron fragment may be used as a protecting group since coordination of a conjugated diene leads to a decreased reactivity of the resulting transition metal complex in which the diene does not undergo hydrogenation or Diels–Alder cycloaddition. Moreover, highly reactive molecules containing labile diene systems can be stabilized. The coordination to the tricarbonyliron fragment prevents the Diels–Alder dimerization of cyclobutadiene and cyclopentadienone as well as the aromatization of cyclohexa-2,4-dien-1-one and 4b,8a-dihydrocarbazol-3-one. Because of its steric demand the tricarbonyliron fragment is often utilized as a stereodirecting group.

Over recent years the reactivity of tricarbonyliron complexes of acyclic butadienes[3] and cyclohexadienes[2,4] has been extensively investigated resulting in a broad range of synthetic applications. This review describes some of the recent advances directed towards the application of tricarbonyl(η⁴-diene)iron complexes to organic synthesis.

2 Selective complexation of dienes by the tricarbonyliron fragment

The standard protocol for the synthesis of tricarbonyl(η⁴-diene)iron complexes involves either thermal or photochemical reaction of the diene with pentacarbonyliron, nonacarbonyldiiron, or dodecacarbonyltriiron. However, complexations are achieved under much milder reaction conditions by using tricarbonyliron transfer reagents.[5] The (η⁴-1-azabuta-1,3-diene)tricarbonyliron complexes **2** represent useful tricarbonyliron transfer reagents. They are easily prepared in high yields from the corresponding 1-azabuta-1,3-dienes **1** on sonication with nonacarbonyldiiron. On reaction of complex **2** with cyclohexa-1,3-diene **3** at elevated temperatures the metal fragment is transferred and provides the tricarbonyliron–cyclohexadiene complex **4** in excellent yield (Scheme 1).[6]



Scheme 1

A highly efficient catalytic complexation of conjugated dienes was developed by reaction with either pentacarbonyliron

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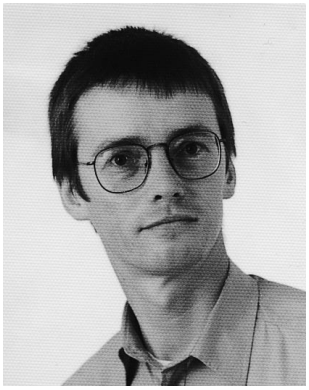
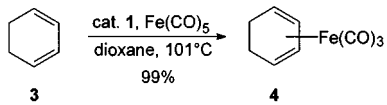


or nonacarbonyldiiron in the presence of the 1-azabuta-1,3-diene **1**. Thus, the 1-azabuta-1,3-diene-catalyzed complexation of cyclohexa-1,3-diene **3** with pentacarbonyliron affords complex **4** quantitatively (Scheme 2).[7]

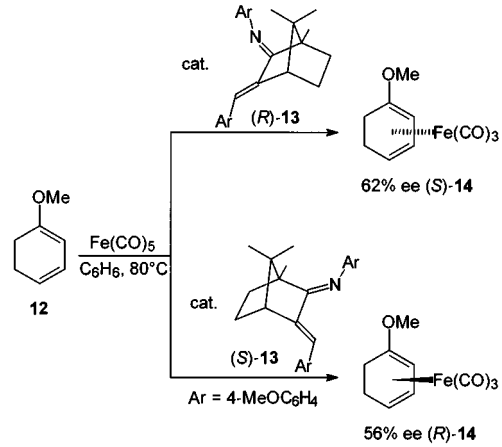


Scheme 2

The catalytic complexation of cyclohexadiene **3** is proposed to be initiated by a nucleophilic attack of the imine nitrogen of the 1-azabutadiene **1** at one of the carbonyl ligands of pentacarbonyliron (Scheme 3).[7] Loss of carbon monoxide by internal ligand displacement transforms the resulting (carbamoyl)tetracarbonyliron complex **5** into the (η^3-allyl) (carbamoyl)tricarbonyliron complex **6**. Complex **6** isomerizes by haptotropic migration of the tetracarbonyliron fragment first to the (η^2-olefin)tetracarbonyliron complex **7** and then to the (η^1-imine)tetracarbonyliron complex **8**. Further loss of a carbonyl ligand from **8** generates the (η^1-imine)tricarbonyliron complex **9**, which is in equilibrium with the stable (η^4-1-azabutadiene)-tricarbonyliron complex **2** (*cf.* Scheme 1) by haptotropic migration of the tricarbonyliron fragment. Reaction of the tricarbonyliron complex **2** with excess pentacarbonyliron leads to the hexacarbonyldiiron complex **11**, which was structurally confirmed by X-ray analysis.[7] The vacant coordination site of the crucial 16-electron intermediate **9** may be filled by η^2-coordination of cyclohexadiene **3** to provide complex **10**. Loss of the 1-azabutadiene regenerates the catalyst **1** and haptotropic ($\eta^2 \rightarrow \eta^4$) migration of the tricarbonyliron fragment affords complex **4**.

Optically active planar chiral tricarbonyliron–diene complexes can be obtained directly by catalytic asymmetric complexation of the corresponding prochiral ligands with the transition metal fragment. Using chiral 1-azabuta-1,3-dienes in the catalytic complexation described above an enantioselective coordination of prochiral 1,3-dienes to the tricarbonyliron fragment with useful asymmetric inductions was achieved.[8] Catalytic complexation of 1-methoxycyclohexa-1,3-diene (**12**) with pentacarbonyliron using the (*R*)-camphor-derived 1-azadiene (*R*)-**13** afforded the tricarbonyliron complex (*S*)-**14**, while catalyst (*S*)-**13** led to complex (*R*)-**14** (Scheme 4).

Current research in this area focusses on the development of more efficient chiral catalysts useful for the asymmetric



Scheme 4

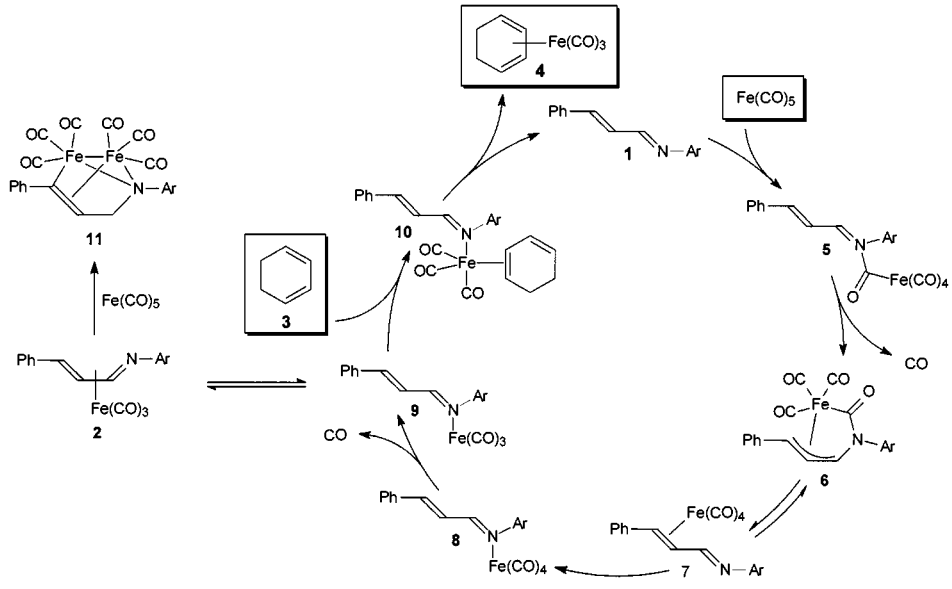
catalytic complexation of a broad range of prochiral buta-1,3-diene and cycloalka-1,3-diene ligands. Thus, this method should facilitate the access to chiral nonracemic tricarbonyliron–diene complexes as starting materials for enantioselective organic synthesis.

3 Applications of tricarbonyliron–butadiene complexes

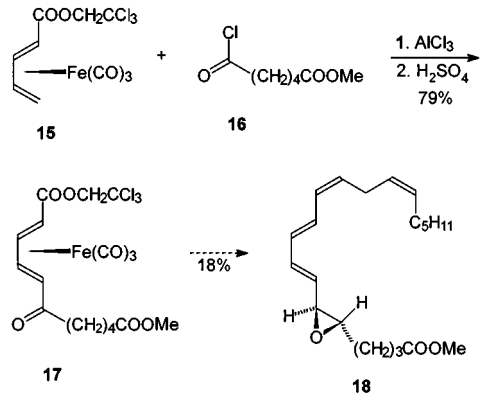
Acyclic tricarbonyliron–butadiene complexes represent useful starting materials for the synthesis of acyclic polyunsaturated natural products, *e.g.* the metabolites resulting from the 5-lipoxygenase pathway of the arachidonic acid cascade.[3]

The stereoselective Friedel–Crafts acylation of tricarbonyliron–butadiene complexes initially affords the *Z*-dienones, which on acid-catalyzed isomerization provide the thermodynamically more stable *E*-dienones.[9] This method was applied to an enantioselective total synthesis of the natural leukotriene (−)-5(*S*),6(*S*)-LTA_4 methyl ester (**18**) (Scheme 5).[10] Friedel–Crafts acylation of the enantiopure iron complex of *trans*-penta-2,4-dienoic 2,2,2-trichloroethyl ester **15** using the acid chloride of adipic acid monomethyl ester afforded complex **17** which was subsequently converted to the LTA_4 methyl ester **18**.

The planar chiral complex tricarbonyl[η^4-methyl (2*E*,4*E*)-6-oxohexa-2,4-dienoate]iron (**19**) is easily separated into the enantiomers by resolution with ephedrine.[11,12] Starting from this chiral building block an eight-step enantioselective total

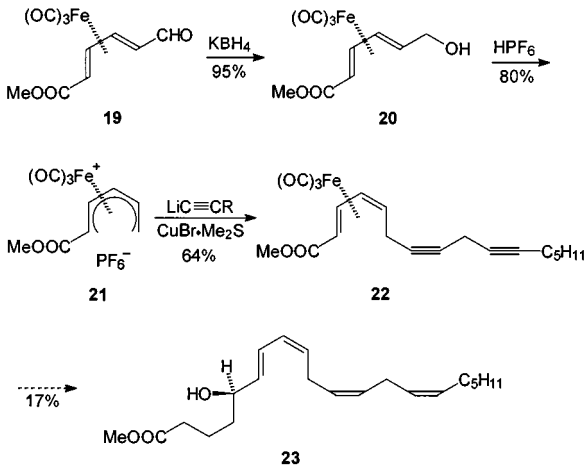


Scheme 3



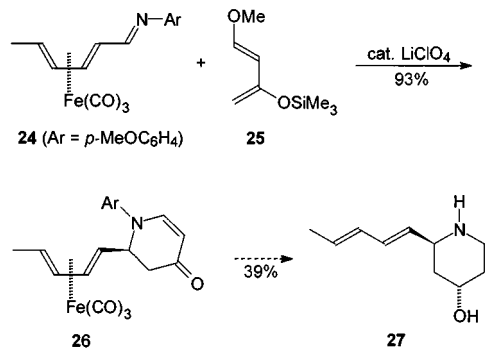
Scheme 5

synthesis of 5(*R*)-hydroxyeicosatetraenoic acid (HETE) methyl ester (**23**) was recently accomplished (Scheme 6).[12] Borohydride reduction of the (−)-complex **19** followed by treatment of the intermediate alcohol **20** with hexafluorophosphoric acid



Scheme 6

afforded the enantiopure 1(*R*)-tricarbonyl[1-(methoxycarbonyl)pentadienylium]iron hexafluorophosphate **21**. Addition of the organocuprate prepared from deca-1,4-diyne occurred with complete regioselectivity and provided the 2(*R*)-methyl (2*E*,4*Z*)-hexadeca-2,4-diene-7,10-diynoate complex **22**. The next steps involve conversion to the (7*Z*,10*Z*)-diene system by stereoselective hydrogenation using Lindlar catalyst, transformation of the ester function into the aldehyde by DIBAL reduction followed by oxidation with manganese dioxide, and nucleophilic addition of a C_4-building block containing a protected ester function (2 : 1 stereoselectivity). The synthesis of 5(*R*)-HETE methyl ester **23** was completed by demetallation of the complex using ceric ammonium nitrate. Current applications of the iron-complexed methyl (2*E*,4*E*)-6-oxo-hexa-2,4-dienoate **19** focus on the enantioselective total synthesis of macrolactin A.[13,14]

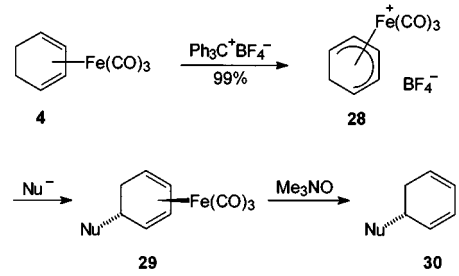


Scheme 7

The first asymmetric synthesis of the piperidine alkaloid SS20846A (**27**) was achieved by a diastereoselective lithium perchlorate-promoted cycloaddition of the enantiopure tricarbonyliron-complexed 1-azatriene **24** with Danishefsky's diene **25** (Scheme 7).[15] The resulting enone **26** was reduced to the saturated alcohol. The final oxidation using ceric ammonium nitrate resulted in simultaneous demetallation of the butadiene moiety and deprotection of the nitrogen atom.

4 Applications of tricarbonyliron–cyclohexadiene complexes

The most characteristic feature of tricarbonyl(η^4-1,3-diene)iron complexes is the activation of the allylic C–H bonds which enables hydride abstraction by triphenylmethyl tetrafluoroborate. Thus, cyclohexa-1,3-diene (**3**) is transformed *via* the tricarbonyliron complex **4** to the tricarbonyl(η^5-cyclohexadienylium)iron tetrafluoroborate (**28**). For steric reasons the bulky tricarbonyliron fragment of the metal-coordinated cation exhibits a strong stereodirecting effect, which on reaction with nucleophiles results in an approach of the reagent from the face opposite to the iron (*anti* selectivity). Therefore, reaction of the complex salt **28** with appropriate nucleophiles provides the 5-*anti*-substituted tricarbonyl(η^4-cyclohexa-1,3-diene)iron complexes **29** by regio- and stereoselective formation of carbon–carbon or carbon–heteroatom bonds. Demetallation of the complexes **29** using trimethylamine *N*-oxide affords the free dienes **30** which are substituted in the allylic position (Scheme 8). Because of the high degree of regio- and stereoselectivity in bond forming reactions at the coordinated ligand this chemistry has found diverse applications in synthetic organic chemistry including natural product synthesis.[2,4]



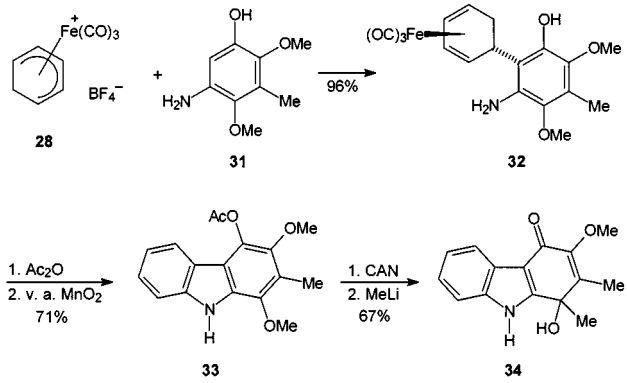
Scheme 8

4.1 Total synthesis of carbazole alkaloids

Over the past two decades a broad range of carbazole alkaloids with useful biological activities were isolated from diverse natural sources.[16] A highly convergent access to these natural products was developed based on consecutive iron-mediated C–C and C–N bond formation.[17] The tricarbonyliron-complexed cyclohexadienyl cations represent very efficient reagents for the electrophilic aromatic substitution of arylamines.[18] Oxidative cyclization of the resulting arylamine-substituted tricarbonyl(η^4-cyclohexa-1,3-diene)iron complexes provides carbazoles. Different techniques for the oxidative cyclization to carbazole derivatives were elaborated depending on the substitution pattern of the arylamine.

The oxidative cyclization of arylamine-substituted tricarbonyl(η^4-cyclohexa-1,3-diene)iron complexes to the 9*H*-carbazoles can be performed as a one-pot transformation with concomitant aromatization and demetallation by using *very active manganese dioxide* (iron-mediated arylamine cyclization). An application of this method was shown by the five-step synthesis of the antibiotic carbazomycins G and H.[19] These

novel carbazole alkaloids isolated from *Streptoverticillium ehimense* are structurally unique because of the quinol moiety. The electrophilic substitution of the arylamine **31** with the complex salt **28** to the iron complex **32** demonstrates that even hexasubstituted arylamines can be generated in this transformation (Scheme 9). After protection by chemoselective *O*-

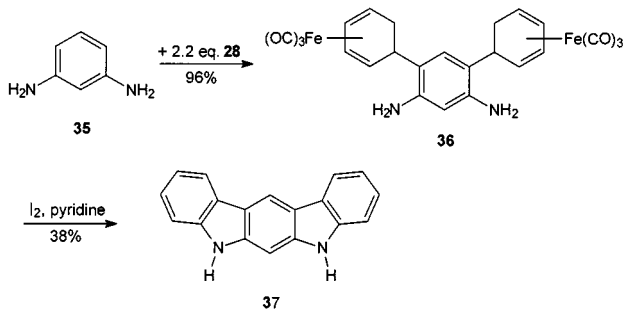


Scheme 9

acetylation an iron-mediated arylamine cyclization to the carbazole **33** was achieved by treatment with very active manganese dioxide. Oxidation of **33** with ceric ammonium nitrate (CAN) to the quinone and subsequent addition of methyllithium afforded carbazomycin G (**34**). Starting from the 3-methoxy-substituted complex salt carbazomycin H became available following the same reaction sequence.

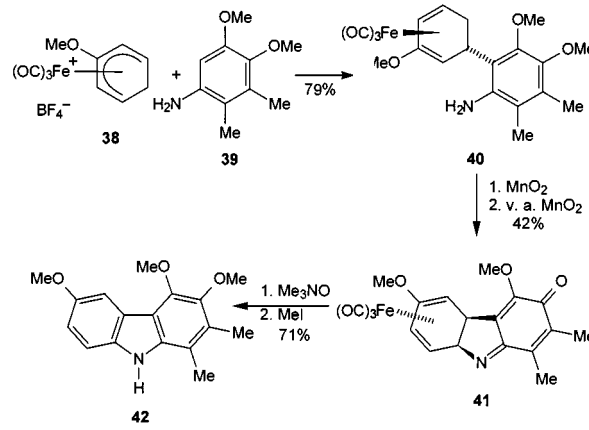
The iron-mediated arylamine cyclization with concomitant aromatization was recently also applied to the total synthesis of the marine natural product hyellazole,[20] the furo[3,2-*a*]carbazole alkaloid furostifoline,[21] and the 5-lipoxygenase inhibitor carbazomycin C.[22]

An extension of this methodology using a two-directional synthesis by simultaneous annulation of two indole units at a central phenylenediamine opens up a simple two-step route to indolocarbazoles (Scheme 10).[23] Two-fold electrophilic substitution of commercial *m*-phenylenediamine (**35**) by reaction with 2.2 equivalents of the complex salt **28** afforded the dinuclear iron complex **36**. Double iron-mediated arylamine cyclization of **36** by oxidation with an excess of iodine in pyridine provided indolo[2,3-*b*]carbazole (**37**).



Scheme 10

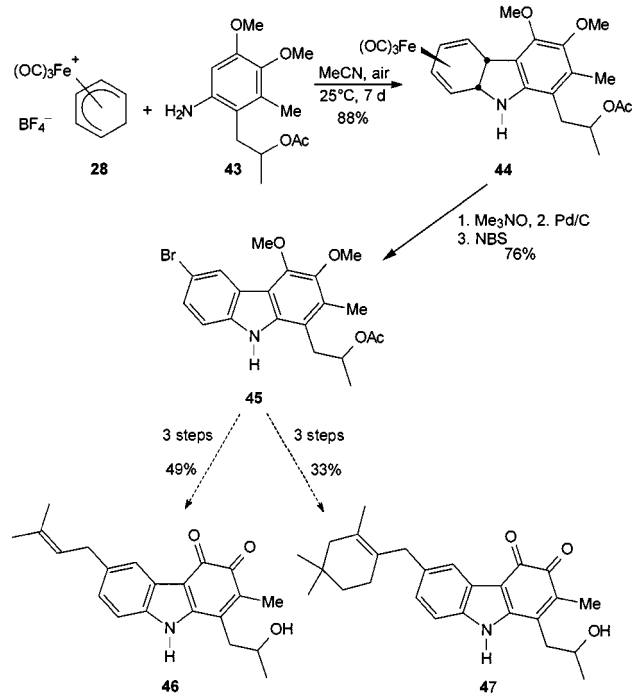
An alternative procedure for oxidative cyclization of the arylamine-substituted tricarbonyl(η⁴-cyclohexa-1,3-diene)iron complexes is the iron-mediated quinone–imine cyclization.[24] Application of this procedure to the total synthesis of the antibiotic carbazomycin D required a regioselective cyclization at an unsymmetrically substituted cyclohexadiene ligand (Scheme 11).[22] Reaction of the 3-methoxy-substituted complex salt **38** with the arylamine **39** provided the iron complex **40**. Chemoselective oxidation of the aromatic nucleus to the quinone imine followed by oxidative cyclization gave the tricarbonyliron-complexed 6-methoxy-substituted 4b,8a-dihy-



Scheme 11

drocarbazol-3-one **41**. The regioselectivity of this oxidative cyclization could be rationalized by previous studies using deuterium-labelled cyclohexadiene ligands.[25] Treatment with manganese dioxide as a two-electron oxidant initially leads to cyclization by exclusive attack of the amino group at C-4 of the cyclohexadiene ligand. The proton-catalyzed rearrangement of this kinetic product, the 8-methoxy isomer, leads to the 6-methoxy isomer **41** and is controlled by the regio-directing effect of the 2-methoxy substituent of the intermediate iron-complexed cyclohexadienyl cation. Demetallation of complex **41** and subsequent *O*-methylation of the intermediate 3-hydroxycarbazole provided carbazomycin D (**42**).[22]

The iron-mediated quinone–imine cyclization is of broad scope and currently provides the best route to 3-hydroxycarbazole alkaloids.[24] Further recent applications of this method in the total synthesis of biologically active carbazole alkaloids include the marine alkaloid hyellazole[20] and the free radical scavenger carazostatin.[26]



Scheme 12

More recently, a third method for oxidative cyclization of the arylamine-substituted tricarbonyliron–cyclohexadiene complexes to the carbazole framework was developed. Oxidation of the iron complexes in acidic medium by molecular oxygen provides selectively the tricarbonyliron-complexed 4a,9a-dihydro-9*H*-carbazole derivatives. The first synthesis of mukonidine

was accomplished by this method.[27] The electrophilic substitution of the arylamine by the iron-complexed cyclohexadienyl cation can be combined with the oxidative cyclization in the air, thus providing access to the carbazole skeleton in a one-pot process. This novel construction of the carbazole framework was applied to the total syntheses of the potent neuronal cell protecting substances (±)-carquinostatin A (**46**)[28] and (±)-lavanduquinocin (**47**)[29] isolated by Seto *et al*. from *Streptomyces* (Scheme 12). The reaction of the arylamine **43** with the complex salt **28** in the air for 7 days at room temperature provided with concomitant oxidative cyclization the tricarbonyliron-complexed 4a,9a-dihydro-9*H*-carbazole **44**. Demetallation of complex **44** followed by dehydrogenation and electrophilic bromination afforded the bromocarbazole **45** which represents a crucial precursor for the total synthesis of 6-allyl-substituted carbazole-3,4-quinone alkaloids. A nickel-mediated coupling with prenyl bromide (for **46**)[28] or with β-cyclolavandulyl bromide (for **47**)[29] respectively, followed by cleavage of the acetate and oxidation with CAN afforded the natural products.

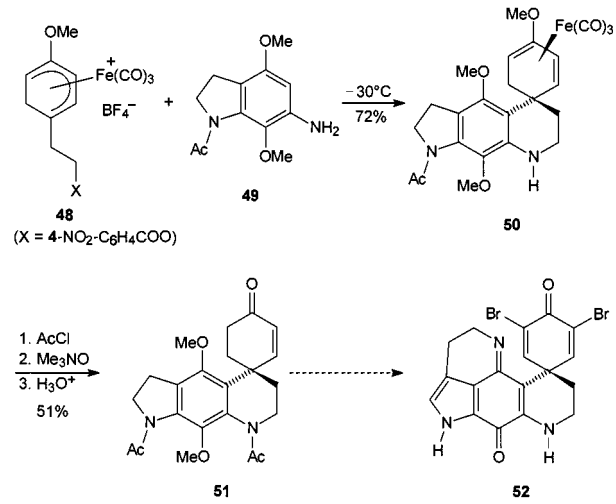
The one-pot construction of the carbazole framework was also used for the first total syntheses of the potent lipid peroxidation inhibitor carbazoquinocin C[30] and the free radical scavenger (±)-neocarazostatin B.[31]

4.2 Diastereoselective spiroannulations

The addition of nucleophiles to tricarbonyl(η^5-1-alkyl-4-methoxycyclohexadienyl)iron cations offers a simple method for the stereoselective generation of quaternary carbon centers. The observed selectivity is a consequence of the regiodirecting effect of the methoxy-substituent, which directs the incoming nucleophile to the 1-position (*para* selectivity), and the stereodirecting effect of the tricarbonyliron moiety, which enforces an attack of the nucleophile from the face opposite to the transition metal (*anti* selectivity).[2,4] Based on this chemistry a diastereoselective one-pot annulation of different spiroquinoline ring systems was developed by reaction of the iron complex salt **48** with arylamines.[4] The complex salt **48** is readily prepared in 50–60% overall yield starting from *p*-methoxyphenylacetic acid by the following simple six-step sequence: 1. Birch reduction, 2. esterification, 3. complexation with pentacarbonyliron, 4. DIBAL reduction, 5. acylation with *p*-nitrobenzoylchloride, and 6. hydride abstraction using triphenylmethyl tetrafluoroborate. The cyclohexadienyl cation of **48** represents a 1,3-double acceptor, since it has a leaving group at a C_2-side chain in the 1-position. Therefore, stereoselective construction of a quarternary carbon by regioselective electrophilic aromatic substitution at the *o*-amino position of the arylamine and subsequent cyclization *via* nucleophilic displacement of the *p*-nitrobenzoate by the amino group provide directly benzo-annulated 3-azaspiro[5.5]undecanes.[4]

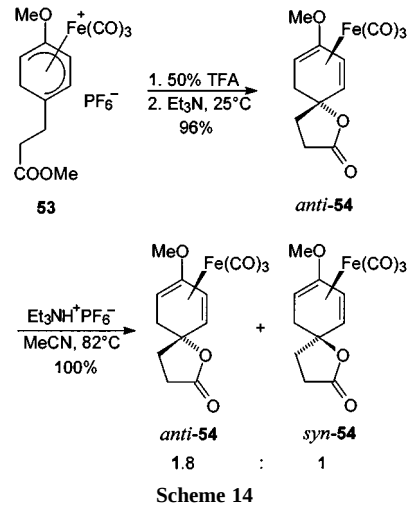
The iron-mediated spiroannulation was used for a synthetic approach to the discorhabdin alkaloids.[32] The discorhabdins are the major cytotoxic pigments isolated from marine sponges of the genus *Latrunculia*. They contain an unprecedented pyrrolo-[1,7]phenanthroline framework with a spiroannulated cyclohexenone ring and exhibit strong cytotoxic and antimicrobial activities. Reaction of the iron complex salt **48** with 1-acetyl-6-amino-4,7-dimethoxyindoline (**49**) at −30 °C afforded diastereoselectively the spirocyclic iron complex **50** in 72% yield (Scheme 13). *N*-Acylation of complex **50** followed by demetallation with trimethylamine *N*-oxide and hydrolysis of the enol ether provided the spirocyclohexenone **51**. This product represents a functionalized tetracyclic substructure of the discorhabdins and appears to be a promising precursor for a projected total synthesis of discorhabdin C (**52**).

The stereodirecting effect of the tricarbonyliron fragment leading to an attack of the nucleophile at the cyclohexadienyl



Scheme 13

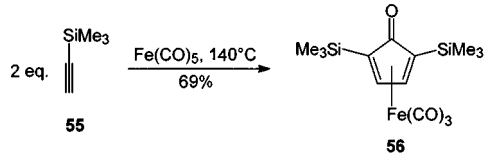
cation exclusively from the face *anti* to the metal (*anti* selectivity) strongly applies only under kinetic reaction conditions. Using thermodynamic reaction conditions for the spirocyclization step, the attack of the nucleophile *syn* to the tricarbonyliron fragment becomes feasible. This reversal of stereoselectivity was demonstrated for the spirolactonization of the complex salt **53** resulting in 3 steps from *p*-methoxycinnamic acid. Cleavage of the ester under acidic conditions and subsequent base-induced cyclization at room temperature stereospecifically provided the spirolactone *anti*-**54** resulting from approach of the carboxylate ion *anti* relative to the tricarbonyliron fragment (Scheme 14). However, application of thermodynamic reaction conditions by refluxing complex *anti*-**54** with triethylammonium hexafluorophosphate in acetonitrile afforded the diastereoisomeric spirolactone complexes *anti*-**54** and *syn*-**54** in a ratio of 1.8 : 1 as the thermodynamic mixture.[33]



Scheme 14

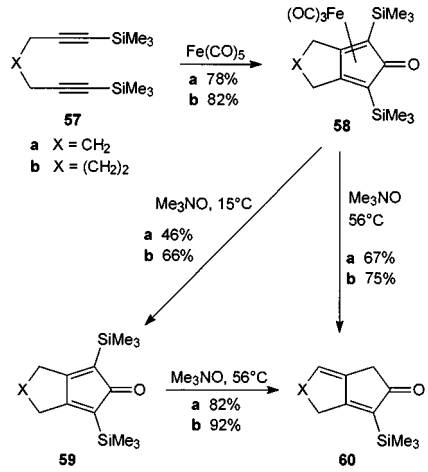
5 Synthesis of cyclopentadienones

The thermal reaction of pentacarbonyliron with alkynes provides tricarbonyl(η^4-cyclopentadienone)iron complexes.[34] This iron-mediated formal [2+2+1] cycloaddition of two alkynes and carbon monoxide was recently reinvestigated.[35−39] Cycloaddition of pentacarbonyliron and two equivalents of trimethylsilylacetylene (**55**) at 140 °C in a sealed tube provided the tricarbonyliron complex of 2,5-bis(trimethylsilyl)cyclopentadienone (**56**) as a single regioisomer (Scheme 15).[35]

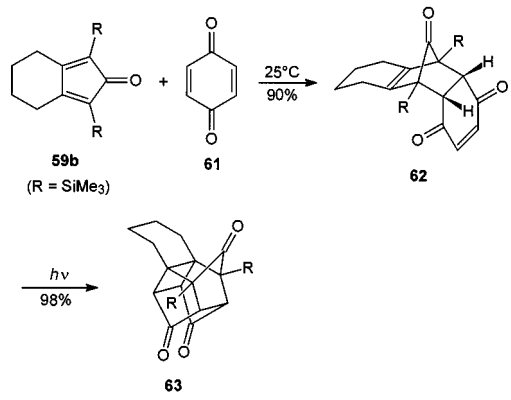


Scheme 15

The bicyclization of the diynes **57** and carbon monoxide by iron-mediated [2+2+1] cycloaddition afforded the tricarbonyliron-complexed bicyclo[*n*.3.0]alkanones **58** (Scheme 16). Variation of the diyne precursor provided a broad range of carbo- and heterobicyclic ring systems.[37] The demetallation of the bicyclic tricarbonyliron(η⁴-cyclopentadienone)iron complexes at low temperature afforded the corresponding cyclopentadienones **59**. At higher temperatures a subsequent double bond isomerization with concomitant monoprotodesilylation provided the dienones **60**.[37] These compounds are potential double Michael acceptors and promise useful applications to the synthesis of cyclopentanoid natural products.



Scheme 16



Scheme 17

Although protected against Diels–Alder dimerization for steric reasons by the two bulky trimethylsilyl substitutents the bicyclic cyclopentadienones **59** represent highly reactive dienes for Diels–Alder cycloadditions with appropriate dienophiles. The Diels–Alder reaction of the bicyclic cyclopentadienone **59b** with *p*-benzoquinone **61** afforded stereoselectively the *endo*-cycloadduct **62** (Scheme 17). A subsequent photochemically initiated intramolecular [2+2] cycloaddition provided quantitatively the hexacyclic cage compound **63**.[40]

6 Conclusion

The 1-azabutadiene catalyzed complexation of dienes with pentacarbonyliron represents a very efficient procedure for the synthesis of tricarbonyliron–diene complexes. Chiral 1-azabutadienes were used for the asymmetric catalytic complexation of prochiral diene ligands providing optically active planar chiral tricarbonyliron complexes. Many enantioselective syntheses of polyunsaturated natural products were elaborated starting from chiral acyclic tricarbonyliron–butadiene complexes. Convergent routes to different natural product frameworks are provided by the tricarbonyliron-mediated annulation of cyclohexadienes and arylamines. The iron-mediated synthesis of carbazoles currently represents the best access to biologically active highly substituted carbazole alkaloids isolated from different S*treptomyces* species over the past years. A one-pot construction of the carbazole framework was achieved by oxidative cyclization in the air and applied to a short and simple route to carbazole-3,4-quinone alkaloids. The diastereoselective iron-mediated spiroannulation of arylamines provided a one-pot access to spiroquinoline derivatives related to the cytotoxic discorhabdin alkaloids. The iron-mediated [2+2+1] cycloaddition of terminally silylated alkynes and carbon monoxide afforded the tricarbonyliron complexes of 2,5-disilylcyclopentadienones. Their free ligands are useful dienes for subsequent cycloadditions to highly substituted cage compounds.

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