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Recent applications of tricarbonyliron-diene complexes to organic synthesis*

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Abstract: The present review describes some of our recent applications of tricarbonyliron-diene chemistry to organic synthesis. It focuses on the selective synthesis of tricarbonyliron-diene complexes including the asymmetric catalytic complexation of prochiral cyclohexa-1,3-dienes, the enantioselective synthesis of carbazole-3,4-quinone alkaloids, and the iron-mediated synthesis of corannulene and yohimbane alkaloids.

INTRODUCTION

Over the past two decades the tricarbonyliron complexes of cyclic as well as acyclic conjugated dienes have found a wide range of applications to organic synthesis [1]. Based on the earlier work reported in two preceding reviews [2,3], we describe herein some more recent developments in the field of tricarbonyliron-diene chemistry achieved by our group [4].

SELECTIVE SYNTHESIS OF TRICARBONYLIRON-DIENE COMPLEXES

The classical method for the coordination of dienes to the tricarbonyliron fragment involves thermal or photochemical reaction with a binary carbonyliron complex, $Fe(CO)_5$, $Fe_2(CO)_9$, or $Fe_3(CO)_{12}$. Due to much milder reaction conditions higher yields are generally achieved by using tricarbonyliron transfer reagents, e.g., $(bda)Fe(CO)_3$ or Grevels' reagent. These compounds are labile complexes in which the ligand exhibits only a relatively weak coordination to the iron [5].

(η^4-1-Azabutadiene)tricarbonyliron complexes as tricarbonyliron transfer reagents

We found that (η^4-1-azabutadiene)tricarbonyliron complexes represent a useful novel class of tricarbonyliron transfer reagents, which are readily available [6,7]. Imine condensation of cinnamaldehyde **1** with the amines **2** affords the 1-azabutadienes **3**, which on ultrasound-promoted reaction with nonacarbonyldiiron provide the (η^4-1-azabutadiene)tricarbonyliron complexes **4** (Scheme 1, Table 1). The transfer of the metal fragment from the complexes **4** to cyclohexa-1,3-diene takes place in tetrahydrofuran under reflux and affords complex **5** after a few hours in high yield. The results summarized in Table 1 emphasize that in this series complex **4b** represents the most efficient tricarbonyliron transfer reagent. The corresponding 1-azabutadiene **3b** can be prepared quantitatively, and the ultrasound-promoted complexation to **4b** proceeds in high yield (88%). Moreover, the reagent **4b** provides complex **5**

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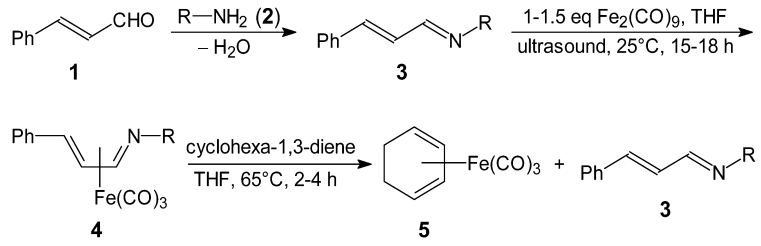


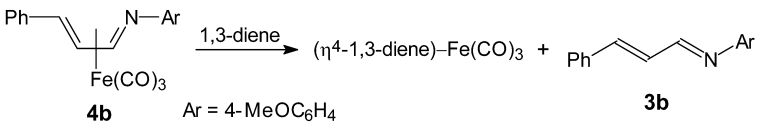
Scheme 1

Table 1 Synthesis of the (η^4-1-azabutadiene)tricarbonyliron complexes **4** and transfer reaction with cyclohexa-1,3-diene.

2	R	**3**, Yield [%]	**4**, Yield [%]	**5**, Yield [%]	Ref.
a	C_6H_5	82	82	88	6
b	4-$MeOC_6H_4$	100	88	95	6
c	2-$MeOC_6H_4$	87	80	74	6
d	2,4-$(MeO)_2C_6H_3$	81	43	80	6
e	$C_6H_5CH_2$	80	76	73	7
f	(*S*)-C_6H_5(Me)CH	92	80	70	7

in 95% yield and after the transfer reaction the free 1-azabutadiene **3b** can be recovered almost quantitatively by recrystallization.

Using complex **4b** as tricarbonyliron transfer reagent a variety of cycloalka-1,3-dienes and buta-1,3-dienes were transformed to their corresponding tricarbonyl(η^4-1,3-diene)iron complexes (Scheme 2, Table 2) [7]. In some cases, higher reaction temperatures were applied to achieve the transfer of the tricarbonyliron fragment in shorter reaction times. However, the attempted reaction of complex **4b** with cyclohexa-1,4-diene did not lead to a transfer of the tricarbonyliron fragment and even using more drastic reaction conditions, only the transfer reagent **4b** was reisolated from the reaction mixture. This result indicated that the (η^4-1-azabutadiene)tricarbonyliron complexes **4** cannot be used for the complexation of 1,4-dienes with concomitant conjugation of the double bonds to tricarbonyl(η^4-1,3-diene)iron complexes. The complexation of 1-methoxycyclohexa-1,3-diene using **4b** afforded the two regioisomeric complexes **6a** and **6b** in a ratio of 1:1.



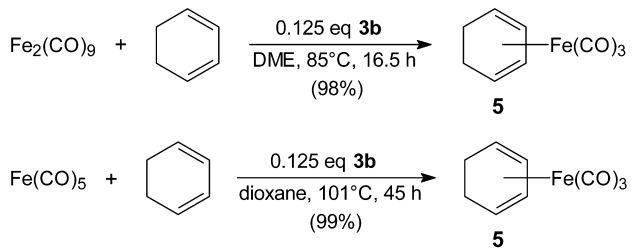
Scheme 2

Table 2 Transfer of the tricarbonyliron fragment from complex **4b** to 1,3-dienes.

1,3-Diene	Reaction conditions	Yield [%] (complex)
cyclohexa-1,3-diene	THF, 65 °C, 2 h	95 (**5**)
cyclohexa-1,4-diene	toluene, 110 °C, 24 h	—
1-methoxycyclohexa-1,3-diene	benzene, 80 °C, 4 h	64 (**6a**/**6b** = 1:1)
cyclohepta-1,3-diene	benzene, 80 °C, 4.5 h	84
2,3-dimethylbuta-1,3-diene	benzene, 80 °C, 25 h	71
sorbic aldehyde	toluene, 110 °C, 1 h	69

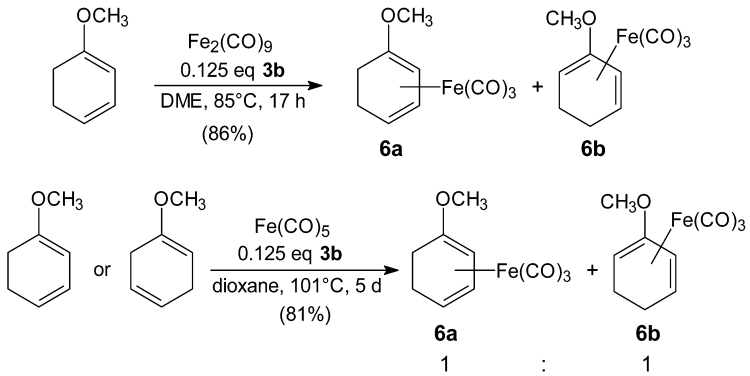
Catalytic complexation of dienes with nonacarbonyldiiron and pentacarbonyliron

Since the free 1-azadiene **3b** was almost completely recovered from the stoichiometric transfer reaction described above, a catalytic version of this reaction appeared feasible. Heating nonacarbonyldiiron and cyclohexa-1,3-diene (1.5 equiv. based on iron) in the presence of 12.5 mol% of **3b** in dimethoxyethane under reflux provided complex **5** in 98% yield based on iron (Scheme 3) [8]. Thus, both of the tricarbonyliron fragments were transferred quantitatively to cyclohexa-1,3-diene. Pentacarbonyliron represents a much cheaper carbonyliron component as starting material, but slightly higher temperatures are required for complete conversion. Using pentacarbonyliron the catalytic complexation of cyclohexa-1,3-diene with the 1-azabutadiene **3b** in dioxane under reflux led also quantitatively to complex **5**. The blank experiments using the same conditions but without catalyst provided complex **5** in 21% (nonacarbonyldiiron) and 8% yield (pentacarbonyliron).



Scheme 3

The catalytic complexation of 1-methoxycyclohexa-1,3-diene using nonacarbonyldiiron and 12.5 mol% of 1-azabutadiene **3b** afforded a mixture of the two regioisomeric complexes **6a** and **6b** in 86% yield based on iron (blank experiment: 24% yield) (Scheme 4) [7]. This result emphasized the feasibility to exploit both tricarbonyliron fragments of nonacarbonyldiiron by the catalytic complexation. Using pentacarbonyliron and 12.5 mol% of **3b** the catalytic complexation of either 1-methoxycyclohexa-1,3-diene or 1-methoxycyclohexa-1,4-diene provided a 1:1 mixture of **6a** and **6b** in 81% yield. Thus, these conditions (pentacarbonyliron, dioxane, reflux) can be applied to the catalytic complexation of 1,4-dienes with concomitant isomerization of the diene system.

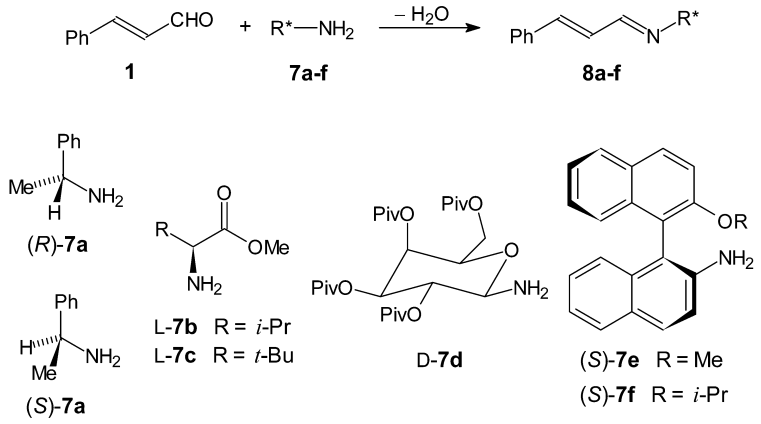


Scheme 4

Asymmetric catalytic complexation of prochiral cyclohexa-1,3-dienes

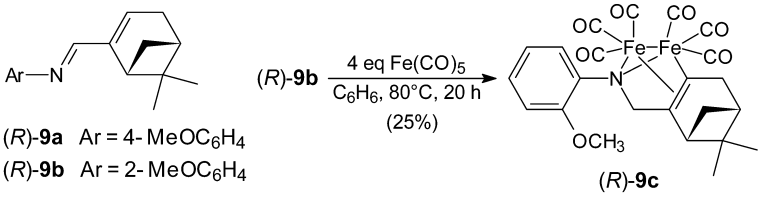
The catalytic complexation of the prochiral ligand 1-methoxycyclohexa-1,3-diene using achiral 1-azabutadiene catalysts provided a racemic mixture of the planar-chiral complex **6a**. With chiral

1-azabutadienes an asymmetric catalytic complexation of prochiral cyclohexa-1,3-dienes could be achieved [9]. The optimization of catalyst and reaction conditions led to a very efficient synthesis of highly enantioenriched planar-chiral tricarbonyl(η^4-cyclohexa-1,3-diene)iron complexes.



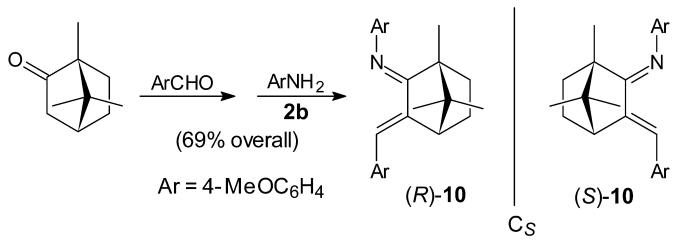
Scheme 5

Three different types of chiral 1-azabutadiene catalysts were prepared and subsequently tested for asymmetric catalysis. Condensation of cinnamaldehyde **1** with the chiral amines **7** provided the chiral 1-azabutadienes **8** (Scheme 5, yields in Table 3) [9–12]. The chiral information can also be located in the aldehyde component. Thus, condensation of (1*R*)-myrtenal with *p*-anisidine **2b** and *o*-anisidine **2c** afforded the catalysts (*R*)-**9a** and (*R*)-**9b** in 62% and 75% yield (Scheme 6) [9]. Reaction of (*R*)-**9b** with pentacarbonyliron in benzene at reflux led to the chiral hexacarbonyldiiron complex (*R*)-**9c**. This dinuclear catalyst was characterized by X-ray analysis [5,11].



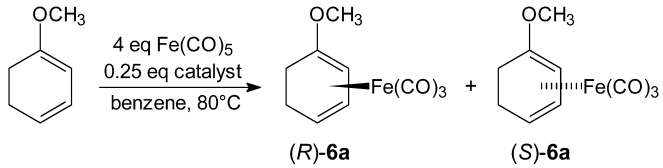
Scheme 6

A third group of chiral catalysts was prepared from chiral ketones by aldol condensation with *p*-methoxybenzaldehyde and subsequent imine condensation with *p*-anisidine **2b**. This sequence was applied to transform (1*R*)- and (1*S*)-camphor to the chiral 1-azabutadienes (*R*)-**10** and (*S*)-**10** (Scheme 7) [9,11]. Their characteristic structural feature is a fixed s-*cis* conformation of the 1-azabutadiene backbone due to the bicyclic terpenoid framework annulated at the 2,3-position.



Scheme 7

To keep the contribution of the uncatalyzed complexation to the product formation as small as possible, the following set of standard reaction conditions was developed for the asymmetric catalytic complexation: 1 equiv. of the prochiral cyclohexa-1,3-diene, 4 equiv. of pentacarbonyliron, and 25 mol% of the chiral catalyst were heated in benzene under reflux. Under these standard reaction conditions the chiral catalysts **8–10** were applied to the asymmetric catalytic complexation of 1-methoxycyclohexa-1,3-diene (Scheme 8, Table 3). In each case, the enantiomeric excess of the planar-chiral tricarbonyl(η^4-cyclohexa-1,3-diene)iron complex **6a** was accurately determined by chiral high-performance liquid chromatography (HPLC) on a commercial β-cyclodextrin column [13]. The blank experiment using the standard conditions without catalyst afforded complex **6a** after 9 days in only 2% yield. Thus, the uncatalyzed complexation leading to racemic **6a** contributes only insignificantly to the product.



Scheme 8

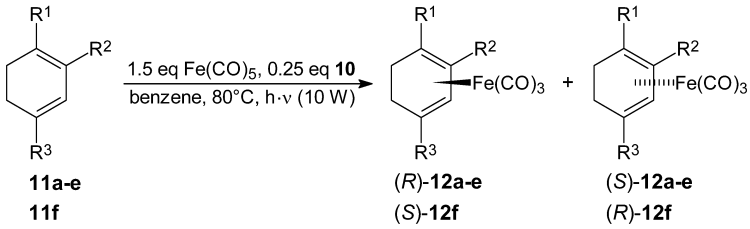
Table 3 Asymmetric catalytic complexation of 1-methoxycyclohexa-1,3-diene with pentacarbonyliron using the chiral 1-azabutadiene catalysts **8–10**.

Catalyst, yield [%]	Reaction time	**6a**, Yield [%]	ee [%][a]	Ref.
—	9 d	2	0	10
(*R*)-**8a**, 92	45 h	68	6 (*S*)	9
(*S*)-**8a**, 92	45 h	69	6 (*R*)	9
L-**8b**, 99	88 h	91	12 (*R*)	10
L-**8c**, 97	67 h	61	15 (*R*)	10
D-**8d**, 53	48 h	38	28 (*R*)	11
(*S*)-**8e**, 90	42 h	87	25 (*R*)	9
(*S*)-**8f**, 46	48 h	81	32 (*R*)	11
(*R*)-**9a**, 62	38 h	29	33 (*R*)	9
(*R*)-**9b**, 75	38 h	67	33 (*R*)	9
(*R*)-**9b**, 75	72 h	95	33 (*R*)	11
(*R*)-**9c**, 25	48 h	47	11 (*R*)	11
(*R*)-**10**, 69	48 h	66	73 (*S*)	12
(*R*)-**10**, 69	12 d	99	73 (*S*)	11

[a]Enantiomeric excess determined by chiral HPLC (absolute configuration of the excess enantiomer) [13].

The 1-phenylethylamine-derived catalysts (*R*)- and (*S*)-**8a** led to an enantiomeric excess of 6% for either enantiomer. The asymmetric induction using the amino acid ester-derived L-**8b** and L-**8c** as catalysts was 12% ee and 15% ee of *R*-**6a**. Better results were obtained with the tetrapivaloyl-β-D-galactopyranosylamine D-**7d**. The asymmetric catalytic complexation of 1-methoxycyclohexa-1,3-diene using D-**8d** afforded **6a** with 28% ee of the *R* enantiomer. However, the efficiency of this catalyst was significantly lower, and complex **6a** was isolated in only 38% yield after 2 days. The axially chiral 1-binaphthyl-1-azabutadienes (*S*)-**8e** and (*S*)-**8f** led to an asymmetric induction in the same range but with 80–90% yield after a reaction time of 2 days. The catalysts (*R*)-**9a** and (*R*)-**9b** with an identical chiral auxiliary provide the same enantiomeric excess of (*R*)-**6a** (33% ee). However, (*R*)-**9b** with a 1-*o*-anisyl substituent exhibits a higher catalytic activity than (*R*)-**9a** with a 1-*p*-anisyl substituent. Thus, using (*R*)-**9b** as catalyst and extension of the reaction time to 3 days afforded complex **6a** in 95% yield

with 33% ee of (*R*)-**6a**. The efficiency of the dinuclear iron complex (*R*)-**9c** as catalyst and the resulting ee are considerably lower. The (1*R*)-camphor-derived 1-azabutadiene (*R*)-**10** led to the highest asymmetric induction in the catalytic complexation (73% ee of (*S*)-**6a**) and also to quantitative yields, but only after extended reaction times (12 days) [11].



Scheme 9

Table 4 Photolytically induced asymmetric catalytic complexation of the prochiral cyclohexadienes **11** with pentacarbonyliron using the camphor-azadiene catalyst **10**.

					12, using cat. (*R*)-**10**		**12**, using cat. (*S*)-**10**	
11	R^1	R^2	R^3	t [d]	Yield [%]	ee [%][a]	Yield [%]	ee [%][a]
a	OMe	H	H	1	97	86 (*S*)	99	85 (*R*)
b	O*i*-Pr	H	H	3	78	79 (+)	82	81 (–)
c	OMe	H	Me	2	86	72 (*S*)	81	73 (*R*)
d	OMe	H	CH_2COOMe	2	93	50 (*S*)	89	50 (*R*)
e	H	COOMe	H	1	90	76 (–)	87	74 (+)
f	COOMe	H	H	1	81	42 (–)	77	42 (+)

[a]Enantiomeric excess determined by chiral HPLC (absolute configuration or direction for the rotation of the plane of polarized light of the excess enantiomer) [13].

Based on the results described above, mechanistic considerations, and taking advantage of the photolytic induction of the asymmetric catalytic complexation we developed a new set of standard conditions: 1 equiv. of **11**, 1.5 equiv. of pentacarbonyliron, 25 mol% of catalyst (*R*)-**10** or (*S*)-**10**, benzene, reflux, irradiation by a 10 W halogen lamp. This photolytically and thermally induced asymmetric catalytic complexation was applied to a series of prochiral cyclohexa-1,3-dienes **11** (Scheme 9, Table 4) [12]. The yields of the planar-chiral tricarbonyl(η^4-cyclohexa-1,3-diene)iron complexes **12** were generally higher than 80%, and the asymmetric inductions were between 42 and 86% ee. By using either (*R*)-**10** or (*S*)-**10** as catalyst, both enantiomers of the tricarbonyliron complexes **12** are available. Complex **12d** is a versatile precursor for spirocyclic compounds [14].

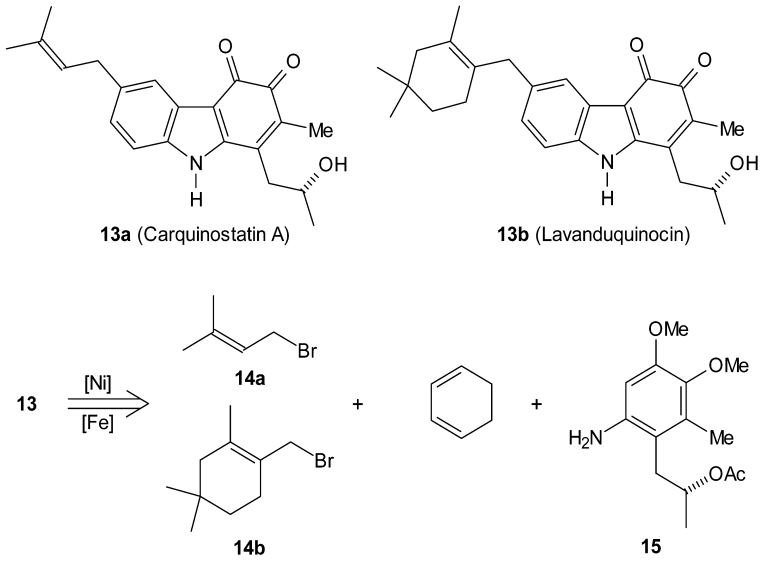
ENANTIOSELECTIVE SYNTHESIS OF POTENT NEURONAL CELL PROTECTING CARBAZOLE-3,4-QUINONE ALKALOIDS

A broad range of carbazole alkaloids with interesting structures and useful biological activities were isolated from different natural sources over the past decades [15]. In 1983, Furukawa isolated the first carbazole-1,4-quinone alkaloids from plants of the genus *Murraya* [15b]. Ten years later, Seto isolated the first carbazole-3,4-quinone alkaloids: carquinostatin A **13a** [16a], isolated from *Streptomyces exfoliatus* 2419-SVT2, and lavanduquinocin **13b** [16b], isolated from *Streptomyces viridochromogenes* 2942-SVS3. These compounds are of interest because they represent potent neuronal cell protecting substances that also exhibit a free-radical scavenging activity. By using the iron-mediated construction

of the carbazole framework we completed the first enantioselective total syntheses of carquinostatin A **13a** [17] and lavanduquinocin **13b** [18].

Retrosynthetic considerations

In the course of our ongoing project directed toward the development of novel methodologies for the total synthesis of biologically active carbazole alkaloids, we became also interested in the carbazole-3,4-quinone alkaloids [19]. The characteristic structural features of **13a** and **13b** are an *ortho*-quinone A-ring, a 2-hydroxypropyl group at C-1, and a terpenoid side chain at C-6.

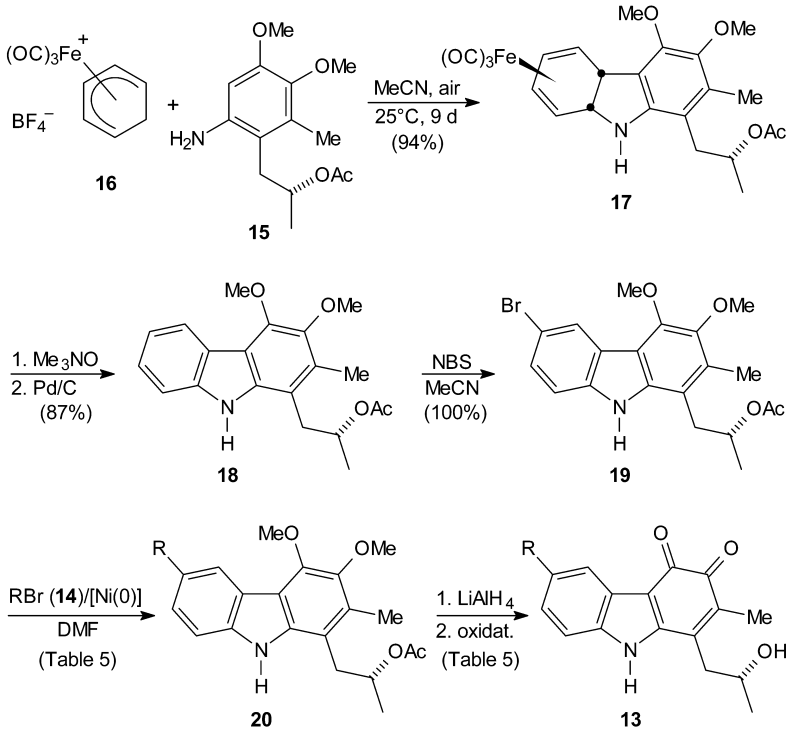


Scheme 10

Our retrosynthetic analysis led to a convergent approach based on the transition metal-mediated couplings of three building blocks (Scheme 10) [17]. Since the two alkaloids **13a** and **13b** differ only in the terpenoid side chain, we envisaged a common 6-bromocarbazole precursor and an introduction of the terpenoid side chain by a nickel-mediated coupling with either prenyl bromide **14a** or β-cyclolavandulyl bromide **14b**. The iron-mediated oxidative coupling of cyclohexa-1,3-diene and the fully functionalized chiral arylamine **15** should provide the carbazole heterocycle.

Total synthesis of carquinostatin A and lavanduquinocin

Starting from commercial 3-methylveratrole and using (*R*)-propene oxide as chiral building block [20], the arylamine **15** was prepared in enantiopure form (5 steps, 57% overall yield) [17]. Hydride abstraction from complex **5** with trityl tetrafluoroborate afforded the complex salt **16** [21]. An oxidative coupling was achieved by stirring the complex salt **16** with 2 equiv. of the arylamine **15** in a solution of acetonitrile at room temperature in the air (Scheme 11). The aromatization of the 4a,9a-dihydrocarbazole iron complex **17** by demetalation and subsequent catalytic dehydrogenation provided the carbazole **18**. Electrophilic bromination afforded the 6-bromocarbazole **19**, which on nickel-mediated coupling [22] with either prenyl bromide **14a** or β-cyclolavandulyl bromide **14b** provided the 6-substituted carbazoles **20a** and **20b** (Table 5). Removal of the acetyl group by reduction and oxidation with cobalt(III) fluoride or ceric ammonium nitrate (Table 5) afforded the alkaloids **13a** [17] and **13b** [18] in an enantiomeric purity of more than 99% ee.



Scheme 11

Table 5 Conversion of the bromo carbazole **19** to carquinostatin A **13a** and lavanduquinocin **13b**.

	R	Coupling conditions	**20**, Yield	Oxidation conditions	**13**, Yield
a	prenyl	$Ni(CO)_4$, DMF, 65 °C	94%	4 eq CoF_3, dioxane/ H_2O, 25 °C	69%
b	β-cyclolavandulyl	$Ni(cod)_2$, DMF, 25 °C	36%	3 eq CAN, MeCN/H_2O, 0 °C	64%

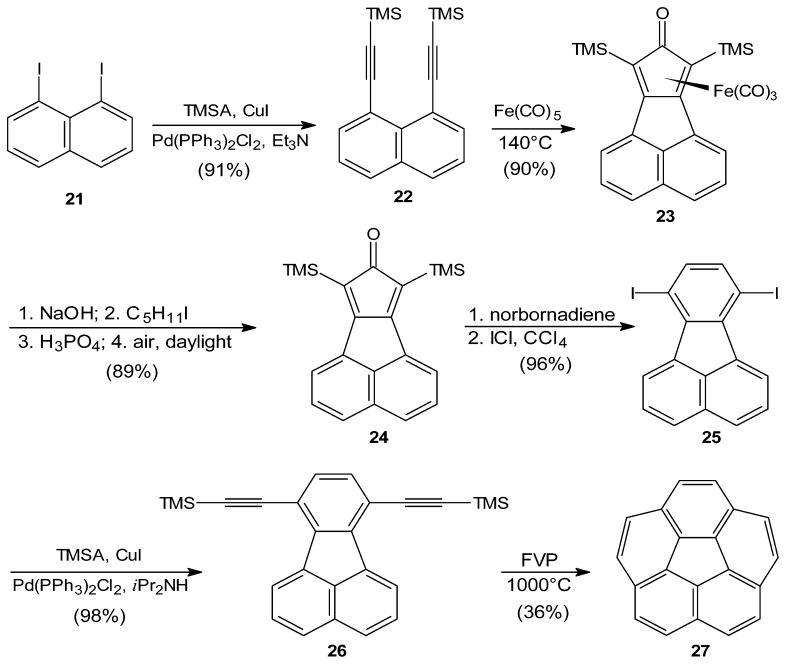
SYNTHETIC APPLICATIONS OF THE IRON-MEDIATED [2+2+1] CYCLOADDITION

Over the past decade we investigated the iron-mediated [2+2+1] cycloaddition of two alkynes and carbon monoxide which provides tricarbonyl(η^4-cyclopentadienone)iron complexes [2,3]. We now demonstrate the utility of this reaction by the first applications to organic synthesis.

Synthesis of corannulene

The smallest bowl-shaped polycyclic unsaturated hydrocarbon fragment of fullerene (C_{60}) is corannulene, which has attracted a lot of synthetic interest [23,24]. We recently applied the iron-mediated [2+2+1] cycloaddition to the synthesis of corannulene (Scheme 12) [25]. The double Sonogashira coupling of 1,8-diiodonaphthalene **21** with monotrimethylsilylacetylene afforded **22**, which on heating with pentacarbonyliron in dimethoxyethane (DME) using a sealed tube provided the complex **23**. Demetalation of this complex was achieved by a novel method developed in our laboratories [26]. Sequential ligand exchange of one carbon monoxide first by a hydrido, then by an iodo ligand, and demetalation of the resulting dicarbonyl(η^5-hydroxycyclopentadienyl)iodoiron complex on contact with air in the presence of daylight led to the cyclopentadienone **24**. Diels–Alder reaction of **24** with norbornadiene followed by electrophilic sub-

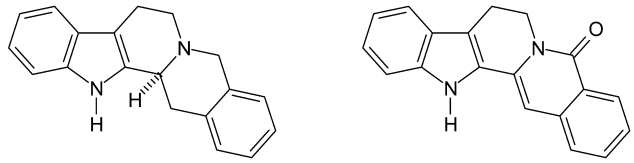
stitution using iodine chloride afforded 7,10-diiodofluoranthene **25**. A double Sonogashira coupling of **25** with monotrimethylsilyl-acetylene (TMSA) gave compound **26**. Flash vacuum pyrolysis of **26** at 1000 °C provided corannulene **27** (7 steps and 25% overall yield).



Scheme 12

Synthesis of (±)-demethoxycarbonyldihydrogambirtannine and norketoyobyrine

The alkaloid (–)-demethoxycarbonyldihydrogambirtannine **28** was isolated first from the leaves of *Ochrosia lifuana* and *Ochrosia miana* (Apocynaceae) (Scheme 13) [27]. Compound **28** is also the main alkaloid of the fruits of *Strychnos usambarensis* (Loganiaceae) found in Africa [28]. These fruits were reported to cause poisoning. Structurally related to (–)-demethoxycarbonyldihydrogambirtannine **28** is norketoyobyrine **29** [29].

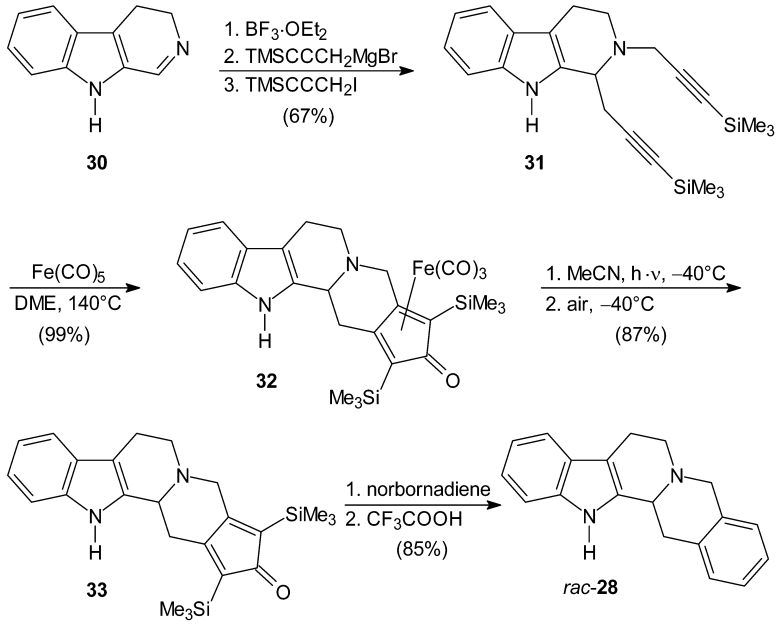


28 (Demethoxycarbonyl-dihydrogambirtannine)

29 (Norketoyobyrine)

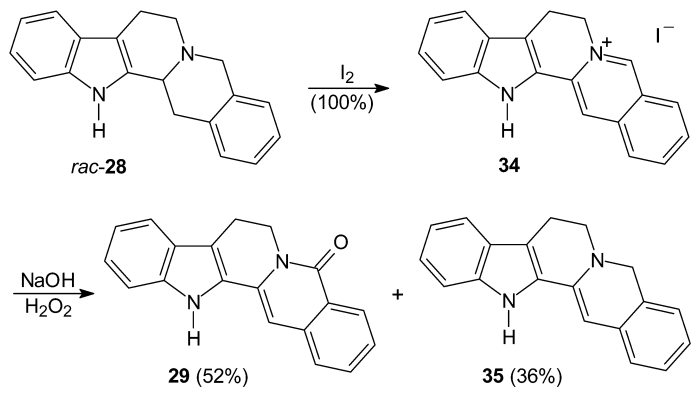
Scheme 13

We projected a total synthesis of the yohimbane alkaloids **28** and **29** based on the iron-mediated [2+2+1] cycloaddition of a 1,2-dipropargyl-1,2,3,4-tetrahydro-β-carboline with carbon monoxide. The aromatic E ring should derive from demetalation of the tricarbonyl(η^4-cyclopentadienone)iron complex and subsequent Diels–Alder cycloaddition with norbornadiene [30].



Scheme 14

The alkylation of 3,4-dihydro-β-carboline **30** with trimethylsilylpropargylmagnesium bromide was achieved in the presence of boron trifluoride (Scheme 14). The subsequent *N*-alkylation with trimethylsilylpropargyl iodide led to 1,2-bis(trimethylsilylpropargyl)-1,2,3,4-tetrahydro-β-carboline **31**. Heating the diyne **31** with 2 equiv. of pentacarbonyliron in 1,2-dimethoxyethane for 20 h at 140 °C in a sealed tube provided quantitatively the tricarbonyl(η^4-cyclopentadienone)iron complex **32** as a 2:1 mixture of two diastereoisomers. An efficient demetalation of the tricarbonyliron complex **32** could be achieved using a novel procedure developed by us previously [31]. Photolytically induced ligand exchange reaction of all three carbon monoxide ligands by acetonitrile and subsequent demetalation of the intermediate triacetonitrile(η^4-cyclopentadienone)iron complex in the air at –40 °C afforded the cyclopentadienone **33** in 87% yield. The Diels–Alder cycloaddition of the cyclopentadienone **33** and norbornadiene in toluene under reflux followed by protodesilylation of both trimethylsilyl groups with trifluoroacetic acid under reflux afforded (±)-demethoxycarbonyldihydrogambirtannine *rac*-**28**. All spectral data of our *rac*-**28** were in full agreement with those reported for the natural product [27,28].



Scheme 15

The present synthesis provides *rac*-**28** in six steps and 49% overall yield based on 3,4-dihydro-β-carboline **30**.

Finally, we describe the transformation of (±)-demethoxycarbonyldihydrogambirtannine *rac*-**28** to norketoyobyrine **29** (Scheme 15) [30]. The dehydrogenation of *rac*-**28** with iodine in ethanol under reflux led to demethoxycarbonylourouparine iodide **34**. Treatment of the iodide **34** with alkaline hydroperoxide under reflux provided norketoyobyrine **29** along with demethoxycarbonylgambirtannine **35**. Spectral data and melting point of norketoyobyrine **29** were in agreement with those described in the literature [29].

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