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Transition Metal-Diene Complexes in Organic Synthesis, Part 27.[1]

Synthesis and Reactivity of 4a,9a-Dihydro-9*H*-carbazoles

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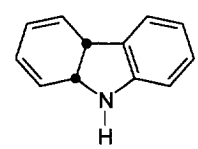
Abstract: A broad range of substituted 4a,9a-dihydro-9*H*-carbazoles is available *via* iron-mediated cyclizations. The chemo- and stereoselectivity of their reactions are described.

Introduction

Bridgehead-dihydro benzo-annulated heteroaromatic ring systems, such as the 4a,9a-dihydro-9*H*-carbazole **1**, are intriguing because of their structural features and so far have been available exclusively by transition metal-mediated processes. The difficulties in getting access to these ring systems by classical procedures arise from the fact that the aromaticity in both rings, the benzo ring and the heteroaromatic one, has been destroyed by the position of the hydrogenation. Therefore, a high tendency to aromatization has to be expected for the corresponding free ligands. However, using a transition metal-mediated reaction as the key step, the 3a,7a-dihydrobenzofuran **2**,[2] the 3a,7a-dihydroindole **3**,[3] the 3a,7a-dihydrobenzimidazole **4**,[4] and the 4a,9a-dihydro-9*H*-carbazole **5**,[5] were obtained as stable compounds (Scheme 1).



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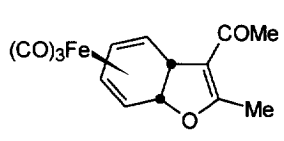

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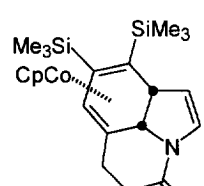

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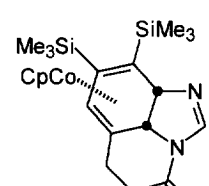

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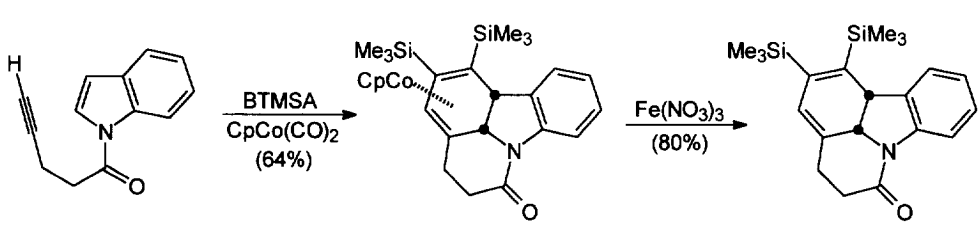


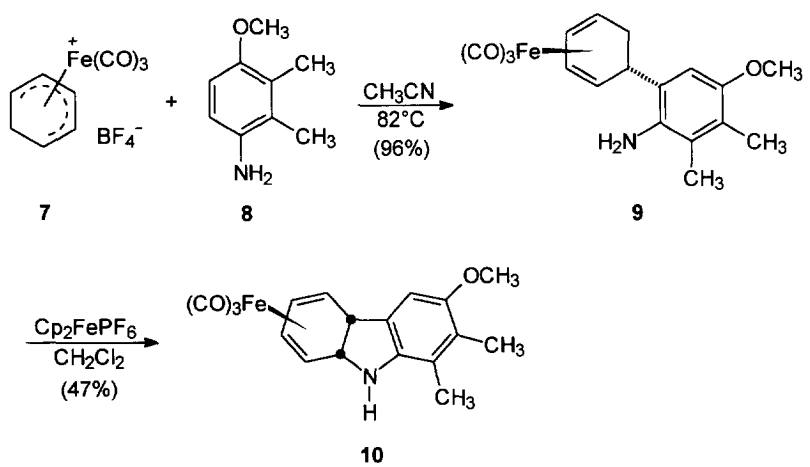
5 **6**

Scheme 1

Obviously, η^4-complexation to a metal fragment, either the tricarbonyliron or the η^5-cyclopentadienylcobalt unit, stabilizes the cyclohexadiene moiety of the molecule and reduces the danger of aromatization. Thus the target structures are provided in their protected form which should deliberate the free ligands on a demetalation process. Vollhardt and coworkers described the syntheses of the complexes **3**, **4**, and **5** by a cobalt-mediated [2+2+2] cycloaddition (*e.g.* 1-[4-pentynoyl]indole with bistrimethylsilylacetylene [BTMSA] to **5**) and demonstrated that in all three cases the corresponding free ligands can be obtained by oxidative demetalation (*e.g.* **5** to **6**).[3-6] In the course of our studies directed towards the iron-mediated total synthesis of biologically active carbazole alkaloids,[7-9] we found two approaches to the 4a,9a-dihydro-9*H*-carbazole ring system which differ in the cyclization mode that has been employed.[10,11] Moreover, our method provides the parent framework without additional annulated rings as in compound **6**. The syntheses of 4a,9a-dihydro-9*H*-carbazoles as well as the chemoselectivity and stereoselectivity of their reactions are reported in this paper.

Synthesis of 4a,9a-dihydro-9*H*-carbazoles *via* selective cyclizing dehydrogenation

The iron complex **9**, a precursor for the synthesis of 4-deoxycarbazomycin B, is obtained in high yield from the 4-methoxy-2,3-dimethylaniline **8** and the iron complex salt **7** by electrophilic aromatic substitution.[10] We proposed tricarbonyliron-complexed 4a,9a-dihydro-9*H*-carbazoles as crucial intermediates of the iron-mediated arylamine cyclization to the aromatized 9*H*-carbazoles.[7] In fact, a highly selective cyclizing dehydrogenation without subsequent aromatization can be achieved by using SET oxidizing reagents with an appropriate oxidation potential, such as ferricenium hexafluorophosphate.[12] This reagent oxidizes complex **9** to an intermediate 17-electron radical cation which is subsequently transformed to the tricarbonyliron-complexed 4a,9a-dihydro-9*H*-carbazole **10** and aromatization is avoided under optimized conditions. Thus, the oxidation of complex **9** with the ferricenium cation selectively provides complex **10** (Scheme 2).[10]



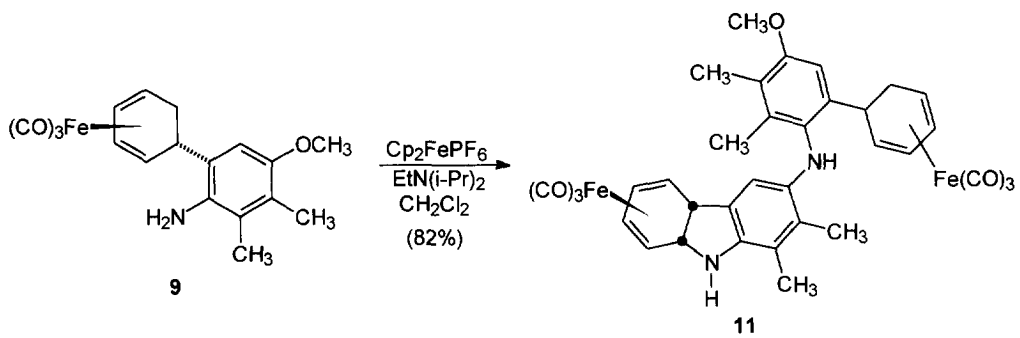
7 **8** **9**

10

Scheme 2

Single crystals of **10** exhibit optical anisotropism. This physical property was explained by the crystal packing where the aromatic rings are arranged in parallel layers.[10] Because of this observation we were interested in getting a broad access to different tricarbonyl[(1-4-η)-4a,9a-dihydro-9*H*-carbazole]iron complexes in order to gather information on the relationship between the physical properties and the structure of these compounds.

In this context we realized two drawbacks of the approach to the 4a,9a-dihydro-9*H*-carbazole iron complex **10** described above. First of all, the reaction depicted in Scheme 2 provided complex **10** only in 47% yield along with 42% of recovered starting material **9**. More than 50% turnover could not be obtained in this cyclization because 1 eq hexafluorophosphoric acid is formed during this process and protonates the starting material and some product. The protonated arylamines were deliberated during workup using *N*-ethyldiisopropylamine. In an attempt to circumvent this problem, the cyclization of complex **9** with the SET oxidizing agent was carried out in presence of the external base *N*-ethyldiisopropylamine(Scheme 3).

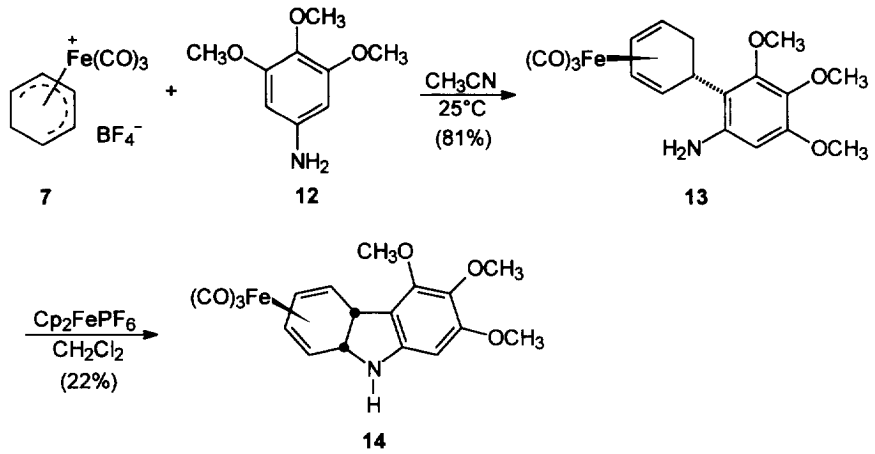


Scheme 3

However, in this case we observed exclusive formation of a dimeric iron complex, which structure has now been tentatively assigned as **11**. Using ferricenium hexafluorophosphate as the oxidizing agent the dimeric complex was obtained in 82% yield as a mixture of diastereoisomers. The same product was formed on oxidation of **9** with iodine in pyridine at room temperature (54% yield) and with lead dioxide in toluene at 80°C (36% yield).[10b] Structural support for **11** derives from its mass spectrum with the peak of the molecular ion at 704 *m/z* and a consistent fragmentation pattern. The ^{1}H-NMR spectrum shows all essential signals including two singlets for the methoxy groups (3.70 and 3.82 ppm) which indicate two diastereoisomers.

The formation of the dimeric complex **11** can be rationalized by nucleophilic attack of the amino group of complex **9** at the aromatic ring of a second molecule which has been oxidized to a nitrenium cation. Products of nucleophilic attack in the *para* position of the arylamine moiety of related iron complexes were previously obtained with alcohols as nucleophiles.[9,13,14] The nucleophilic attack of the first molecule of **9** onto the second one could occur before or after the cyclizing dehydrogenation of the arylamine of the second molecule (*cf.* the examples which were previously reported).[9,13] A reductive rearomatization of a cross-conjugated dienimine subunit of a dihydrocarbazole would represent the final step in the sequence leading to **11**. Such a transformation was previously observed in the course of our total synthesis of murrayafoline A[14] and, in the present case, is probably initiated by ferrocene and hexafluorophosphoric acid.

A further problem with the selective cyclizing dehydrogenation to the iron-complexed 4a,9a-dihydro-9*H*-carbazoles is that the oxidation potential of the precursor is significantly dependent on the substitution pattern of the arylamine moiety. Therefore, ferricenium hexafluorophosphate does not provide optimal results in all cases, which limits the practicality and the scope of this reaction. A further example which was investigated is the complex **13** which results from the electrophilic substitution of 3,4,5-trimethoxyaniline **12** on treatment with the iron-complex salt **7** (Scheme 4).[9]

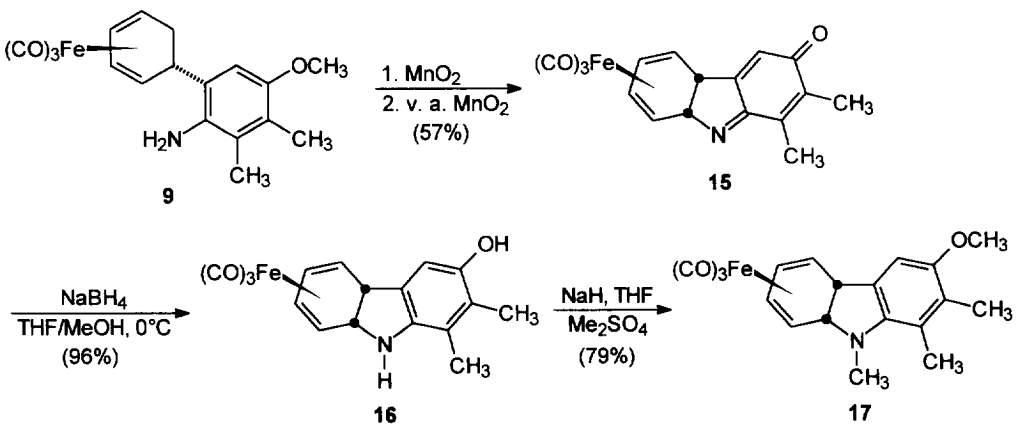


Scheme 4

Oxidative cyclization of complex **13** with ferricenium hexafluorophosphate was performed as described for the synthesis of **10**. However, on the attempt to deliberate protonated product during workup by treatment with *N*-ethyldiisopropylamine decomposition occured. Therefore, the crude product was submitted directly to flash chromatography which reduced the yield. Complex **14** was obtained as yellow crystals and turned out to be extremely sensitive towards oxidation in the air. The structural assignment is based on the characteristic signals of the protons at C4a and C9a in the ^{1}H-NMR spectrum, both appear as a doublet of doublets at 3.91 and 4.32 ppm with a vicinal coupling of $J = 10.8$ Hz (Table 1).

Synthesis of 4a,9a-dihydro-9*H*-carbazoles *via* reduction of 4b,8a-dihydrocarbazol-3-ones

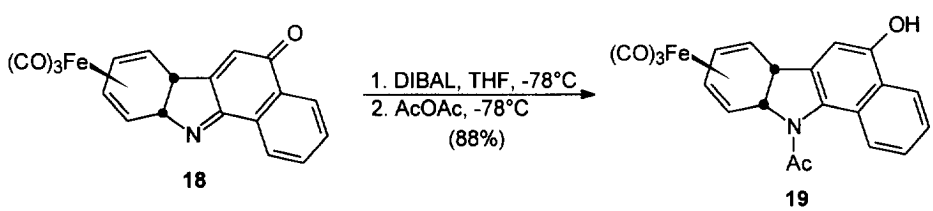
In view of the drawbacks of the chemoselective cyclizing dehydrogenation of the arylamine described above we developed an alternative and much more general approach to the tricarbonyl[(1-4-η)-4a,9a-dihydro-9*H*-carbazole]iron complexes using the iron-mediated quinone imine cyclization (Scheme 5).[11]



Scheme 5

The iron-complexed 4b,8a-dihydrocarbazol-3-one **15** was conveniently prepared by chemoselective oxidation of the arylamine ring of complex **9** to the quinone imine using commercial manganese dioxide followed by the iron-mediated quinone imine cyclization to **15** with very active manganese dioxide.[10] Reduction of the quinone imine ring in **15** was achieved with *in situ* prepared sodium trimethoxyborohydride and provided the 3-hydroxy-4a,9a-dihydro-9*H*-carbazole **16** in 96% yield as colorless crystals. Especially for reactions on a larger scale (more than 250 mg of starting material **15**) low temperature crystallization has proven to be superior to flash chromatography for the purification of complex **16**. The ^{1}H-NMR spectrum confirms the 4a,9a-dihydro-9*H*-carbazole structure by the signals for the C4a and C9a protons at 3.79 and 4.32 ppm with a vicinal coupling of J = 10.8 Hz (Table 1). Deprotonation of **16** with an excess of sodium hydride followed by treatment with an excess of dimethyl sulfate afforded the *N,O*-dimethyl derivative **17** in 79% yield.[11] Solutions of the 4a,9a-dihydro-9*H*-carbazole complex **17** proved to be very labile in the air. Particularly during chromatography on silica gel demetalation with concomitant aromatization to the corresponding 9*H*-carbazole occurs unless the silica gel and the eluents are carefully degassed (Scheme 9). The dimethylation is evident by the signals for the methyl groups in the ^{1}H-NMR spectrum (NCH_3: 2.73 ppm, OCH_3: 3.75 ppm) and in the ^{13}C-NMR spectrum (NCH_3: 43.13, OCH_3: 56.29 ppm). The characteristic C4a and C9a protons at 3.68 and 3.97 ppm exhibit a vicinal coupling of J = 10.5 Hz (Table 1). Single crystals of complex **17** show the same crystal packing and optical anisotropism as previously observed for complex **10** (*vide infra*).

In view of the tremendous synthetic scope of the iron-mediated quinone imine cyclization[9] which provides a broad range of tricarbonyliron-complexed 4b,8a-dihydrocarbazol-3-ones the sequence described above is very promising. Combination of the iron-mediated quinone imine cyclization with the reduction of the quinone ring should open up a general access to the 4a,9a-dihydro-9*H*-carbazoles. In order to demonstrate this feasibility we transformed the 6b,10a-dihydrobenzo[*a*]carbazol-5-one complex **18** into the 6b,10a-dihydro-5-hydroxybenzo[*a*]carbazole complex **19** (Scheme 6).



Scheme 6

Smooth reduction of complex **18** to the corresponding dihydrohydroxycarbazole was achieved with DIBAL at -78°C. Without isolation this product was submitted to dialkylation conditions described above. However the product was too labile to be isolated and characterized. We anticipated, that an electron-withdrawing group should diminish the high tendency of the dihydrocarbazole to undergo aromatization. Therefore, we decided to achieve a direct in situ acetylation by addition of acetic anhydride to the reaction mixture. The new signal in the ^{1}H-NMR spectrum (singlet at 2.24 ppm) and in the ^{13}C-NMR spectrum (CH_3 at 23.21 ppm) as well as the mass spectrum indicate that only monoacetylation took place. The signals of the angular protons at C6b and at C10a appear at 3.99 and 4.90 ppm with a vicinal coupling of J = 9.5 Hz. Comparison of these chemical shifts with those of the corresponding protons of complex **23** confirms the selective *N*-acetylation (Table 1).

The *N*-acetyl derivative **19** does not show optical anisotropism as found for the complexes **10** and **17**.

X-ray crystal structure investigation of the tricarbonyliron complex 17

The stereochemistry of complex **17** (*syn* arrangement of the tricarbonyliron unit and both angular hydrogen atoms at C4a and at C9a) has been additionally confirmed by an X-ray crystal structure analysis (Figure 1).[15] The organic ligand has a vaulted conformation with an angle of 78.9(1)° between the plane of the dihydroindole ring and the diene plane (C1-C4). The metal fragment is bound to the *convex* face.

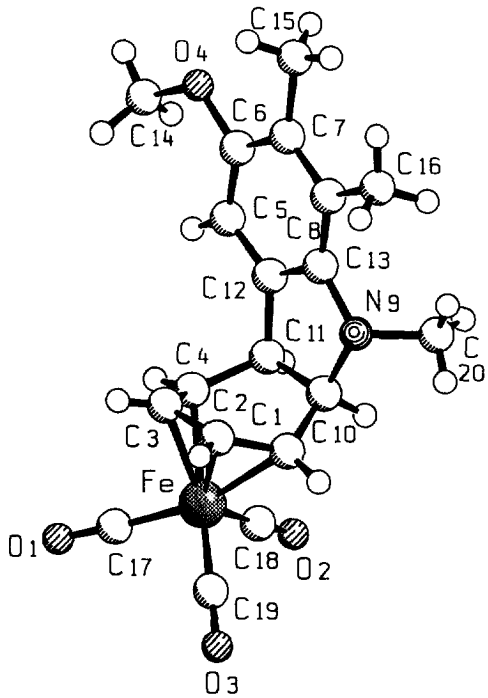
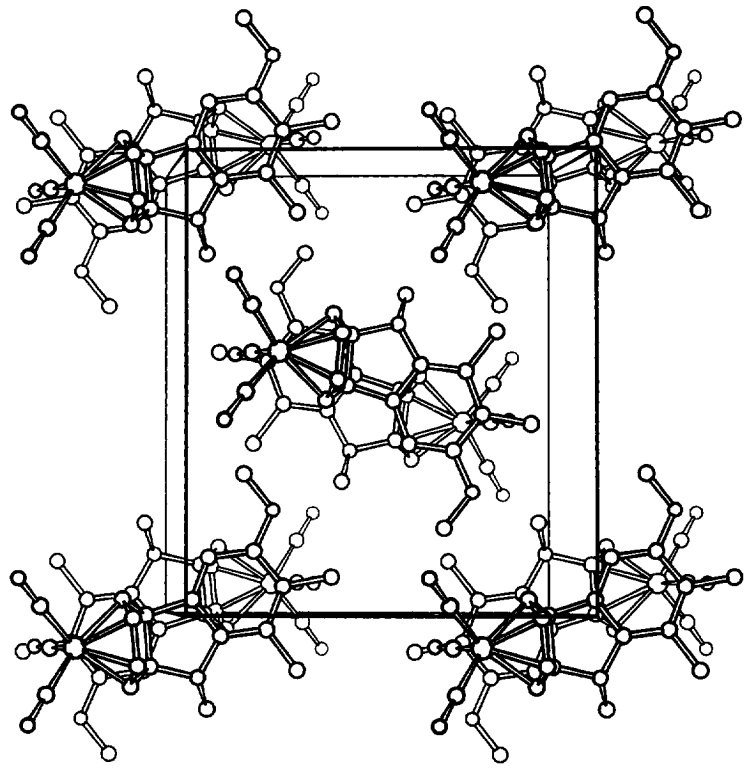
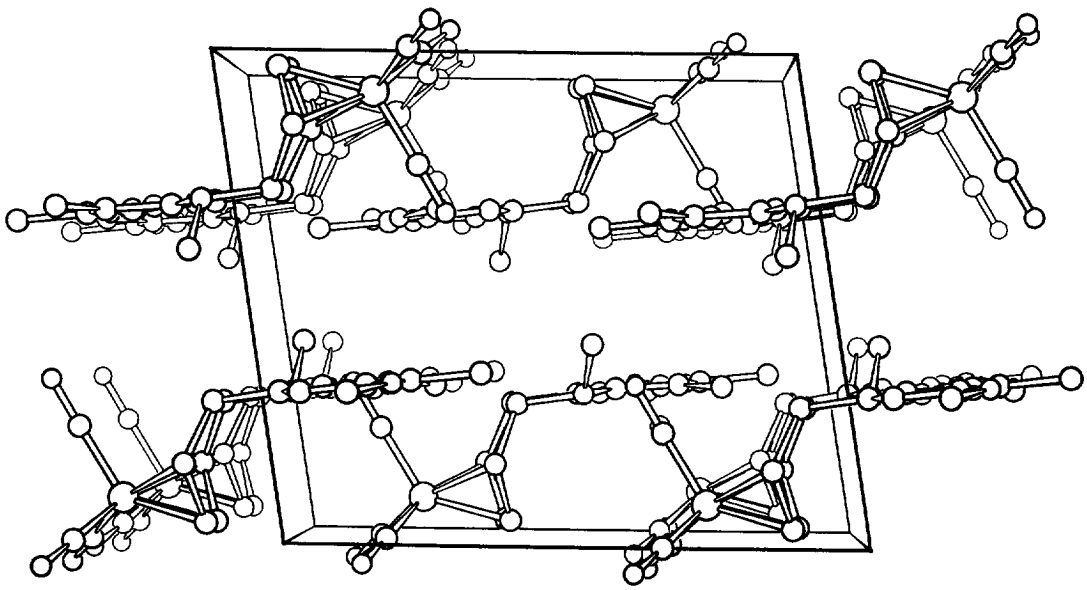


Figure 1. Molecular structure of complex **17** in the crystal (arbitrary numbering). Selected bond lengths [Å]: Fe-C1 2.109(2), Fe-C2 2.063(2), Fe-C3 2.051(2), Fe-C4 2.101(2), C1-C2 1.416(3), C2-C3 1.399(4), C3-C4 1.413(3), C4-C11 1.512(3), C10-C11 1.548(3), C1-C10 1.510(3), N9-C10 1.490(2), N9-C13 1.413(3), C11-C12 1.510(2), C12-C13 1.384(2).

The single crystals of complex **17** exhibit optical anisotropism as found previously for complex **10**, they appear orange-red and yellow at orthogonal planes. This characteristic feature can be explained by the crystal packing (Figure 2). When looking at the plane of the aromatic rings (Figure 2a), the crystals appear orange-red. Looking in plane of the aromatic rings, by rotation of the crystals by 90° about the longitudinal axis (Figure 2b), the crystals appear yellow. The 4a,9a-dihydro-9*H*-carbazole represents columns, where the aromatic rings are arranged in parallel layers with two layers of tricarbonyliron-complexed diene fragments in between them. Exactly the same crystal packing was found for complex **10**, which is lacking the *N*-methyl group, and also the unit cell dimensions are almost identical (see experimental section). The fact, that the *N*-acetyl derivatives **19** and **23** (see below) do not exhibit similar optical properties, demonstrates the significant influence of the substitution pattern of the arylamine moiety.



a)

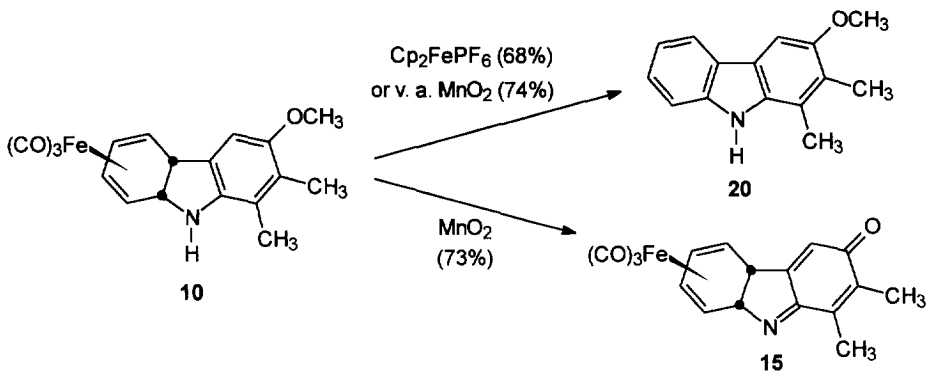


b)

Figure 2. Crystal packing of complex **17**

Chemoselective oxidations of 4a,9a-dihydro-9*H*-carbazoles

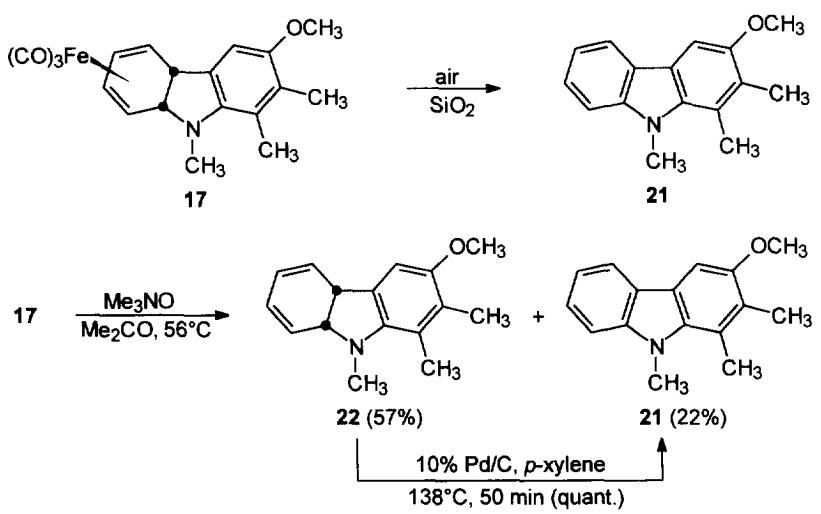
Chemoselective oxidations of the tricarbonyliron complex **10** have already been reported in the course of our total synthesis of 4-deoxycarbazomycin B (**20**).[10] Treatment of **10** with very active manganese dioxide gave **20** in 74% yield along with 9% of complex **15**. Complete chemoselectivity in the sequence dehydrogenation/ aromatization was achieved with ferricenium hexafluorophosphate, which gave **20** in 68% yield (Scheme 7).



Scheme 7

This result indicates that the aromatization, which represents the second step of the iron-mediated arylamine cyclization, like the cyclizing dehydrogenation is initiated by a single-electron transfer and is mediated by the transition metal. Moreover, it becomes clear why an excess of the oxidizing agent in the cyclizing dehydrogenation does not improve the yield of **10** (*cf.* Scheme 2). A chemoselective oxidation of the aromatic nucleus of **10** could also be achieved. Using commercial manganese dioxide, which contains water, the 4b,8a-dihydrocarbazol-3-one complex **15** was obtained in 73% yield along with 8% of the 9*H*-carbazole **20**.

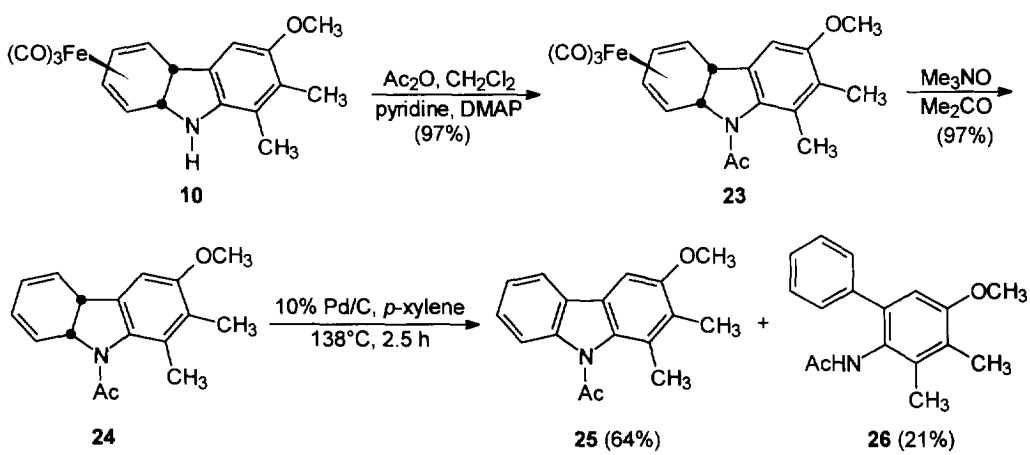
Exploration of the chemistry of the free 4a,9a-dihydro-9*H*-carbazoles required a method for chemoselective demetalation of their tricarbonyliron complexes by avoiding the aromatization. However, the *N*-H derivatives **10** and **14** proved to be extremely labile in solution and underwent unselective oxidation in the air. A chemoselective oxidative demetalation was therefore attempted with the *N*-methyl derivative **17** (Scheme 8).



Scheme 8

Even with complex **17** we realized, that handling of solutions of this compound in the air and especially chromatography on silica gel in the presence of air resulted in complete demetalation with concomitant aromatization to afford the carbazole **21** (4-deoxy-9-methylcarbazomycin B). However, oxidative demetalation of complex **17** by treatment with trimethylamine *N*-oxide[16] under an argon atmosphere in acetone at reflux for 45 min provided the 4a,9a-dihydro-9*H*-carbazole **22** in 57% yield[11] along with the aromatized carbazole **21** (22% yield). The ^{1}H-NMR spectrum confirms the structure assignment for **22** by the signals of the four olefinic protons between 5.74 and 6.06 ppm and of the two angular protons at C4a (4.00 ppm) and C9a (4.16 ppm) with a vicinal coupling of J = 12 Hz. Aromatization of the free ligand **22** to the carbazole **21** was achieved by catalytic dehydrogenation with 10% palladium on carbon in boiling *p*-xylene for 50 min. This method, which proved to be ineffective for the direct aromatization of the tricarbonyliron-complexed 4a,9a-dihydro-9*H*-carbazoles (*e.g.* **10**)[10b] because of steric reasons, is obviously very effective in case of the corresponding free ligands. Thus, a convenient access to a highly reactive 4a,9a-dihydro-9*H*-carbazole was elaborated.

The partial aromatization which occurred on demetalation of complex **17** prompted us to develop an even more selective route to the desired 4a,9a-dihydro-9*H*-carbazoles. In this context we recalled an observation we made in the course of our iron-mediated total synthesis of carbazole alkaloids. An electron-withdrawing substituent at the aromatic nucleus of the arylamine ring enhanced dramatically the stability of the intermediate tricarbonyliron-complexed 4a,9a-dihydro-9*H*-carbazole in iron-mediated arylamine cyclizations. Therefore, following the cyclizing dehydrogenation, additional oxidizing agent (very active manganese dioxide) had to be added in order to achieve aromatization with concomitant demetalation. The oxidative cyclization leading to *O*-acetylcarbazomycinal (see: total synthesis of carbazomycinal, experimental section)[17] and the cyclizations to mukonine and murrayanine (see: total synthesis of 1-oxygenated carbazole alkaloids, experimental section)[14] showed this reactivity of acceptor-substituted derivatives. The stabilizing effect of an *N*-acetyl substituent has been noted above, during the synthesis of the 6b,10a-dihydro-11*H*-benzo[*a*]carbazole framework (Scheme 6). In view of these experimental observations, we decided to elaborate an improved route to the 4a,9a-dihydro-9*H*-carbazole ring system by selective *N*-acetylation of complex **10** prior to demetalation (Scheme 9).



Scheme 9

Acetylation of complex **10** using a standard procedure afforded quantitatively the *N*-acetyl derivative **23**. The introduction of the acceptor-substituent led to a much higher stability of the iron complex, due to the decrease of electron density in the aromatic nucleus, and, as already observed for complex **19**, to a loss of the optical anisotropism. The ^{1}H-NMR spectrum of **23** confirms the structure assignment by the singlet for the acetyl group at 2.04 ppm and by the signals for the C4a and C9a protons at 3.83 and 4.78 ppm (Table 1). The downfield shift of the angular proton at C9a is characteristic of *N*-acetyl derivatives and also confirms the structure assignment of complex **19**.

Table 1. Characteristic ^{1}H-NMR data of tricarbonyl[(1-4-η)-4a,9a-dihydro-9*H*-carbazole]iron complexes (200 MHz, $CDCl_3$)

	10	**14**	**16**	**17**	**19**[a]	**23**	**27**
δ (4a-H)	3.84	3.91	3.79	3.68	3.99	3.85	3.63
δ (9a-H)	4.32	4.32	4.32	3.97	4.90	4.78	3.89
$J_{4a,9a}$ [Hz]	11	10.8	10.8	10.5	9.5	-[b]	10.9

[a] For complex **19** the data of the corresponding protons at C6b and C10 are given; solvent: DMSO-d_6.

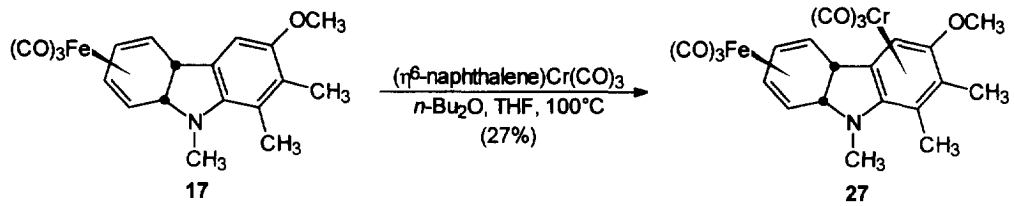
[b] The coupling constant could not be determined (both signals appeared as multiplets).

Demetalation of complex **23** with trimethylamine *N*-oxide provided quantitatively the stable free ligand **24**. The structural assignment is based on the ^{1}H-NMR spectrum which exhibits the signals of the four olefinic protons between 5.61 and 6.10 ppm, the C4a proton at 4.07 ppm, and the C9a proton at 5.43 ppm. Dehydrogenation of **24** with 10% palladium on carbon in boiling *p*-xylene afforded after 2.5 h the carbazole **25** (9-acetyl-4-deoxycarbazomycin B) in 64% yield along with the biphenyl derivative **26** (21% yield), which is formed by ring cleavage.

The *N*-acetyl-4a,9a-dihydro-9*H*-carbazole **24** is considerably more stable than the *N*-methyl derivative **22**. This fact is also reflected by the much more efficient aromatization to the 9*H*-carbazole in a considerably shorter time with the palladium catalyst. The dehydrogenation of the free ligand **24** to the aromatized carbazole **25** is in contrast to the report of Vollhardt and coworkers who described that the tetracyclic *N*-acyl-4a,9a-dihydro-9*H*-carbazole **6** was left unchanged after exposure to 10% Pd/C in boiling *m*-xylene.[5] It remains unclear, whether the additional annulated ring of compound **6** or the bulky trimethylsilyl substituents are responsible for this difference in reactivity.

Stereoselective reactions at 4a,9a-dihydro-9*H*-carbazoles

The remarkable physical properties of the iron complexes **10** and **17** prompted us to develop an access to the corresponding heterodinuclear complexes by complexation with the tricarbonylchromium fragment. However, reaction of complex **17** with hexacarbonylchromium in *n*-Bu_2O/THF (10:1)[18] at 100-120°C for 24 h resulted in decomposition. Transfer of the tricarbonylchromium fragment onto **17** using the method of Kündig[19] by treatment with tricarbonyl(η^6-naphthalene)chromium[20] provided stereoselectively the heterodinuclear complex **27** (Scheme 10).

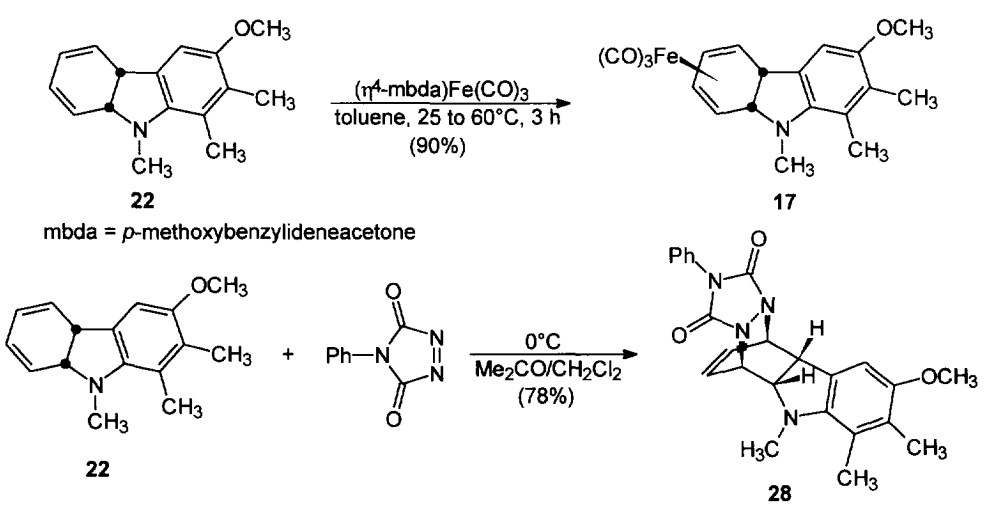


Scheme 10

Structural assignment is based on the mass spectrum which shows the peak of the molecular ion at 517 *m/z* and successive loss of first the tricarbonylchromium fragment and then of the tricarbonyliron fragment with concomitant aromatization (loss of two hydrogens). The infrared spectrum exhibits the CO bands for both metal fragments, the tricarbonyliron unit (2052, 1979, 1969 cm^{-1}) and the tricarbonylchromium unit (1944, 1871, 1845 cm^{-1}). In the ^{1}H-NMR spectrum the signals of two angular protons at C4a and C9a appear in the same region as for complex **17** (Table 1) and the signal for the C5 proton at 5.03 ppm is shifted to higher field. The ^{1}H-NMR spectrum also revealed that a single diastereoisomer was formed.

The 4a,9a-dihydro-9*H*-carbazole framework has a vaulted conformation and therefore, the attack of reagents should take place by approach from the convex face of the molecule. This stereochemical outcome was already observed for diastereoselective allylsilane additions to the 4b,8a-dihydrocarbazol-3-one complex **15**.[11] A similar *exo*/*endo* situation can be realized in the case of the corresponding tricarbonyliron complexes **10** and **17** (*cf.* crystal structure of complex **17**, Figure 1). Thus, a complexation by approach of the tricarbonylchromium fragment from the convex face, *syn* relative to the tricarbonyliron moiety, was assumed and led us to assign the stereochemistry as depicted in structure **27**.

For the reason given above, the same stereochemical outcome was expected for the corresponding free ligand. Approach of the reagent from the convex face of the 4a,9a-dihydro-9*H*-carbazole should lead to the exo substituted products. Our assumption could easily be confirmed by remetalation of **22** with the tricarbonyliron fragment (Scheme 11).



Scheme 11

Recomplexation of the 4a,9a-dihydrocarbazole **22** with tricarbonyl[η^4-4-methoxybenzylideneacetone]iron[21] provided exclusively the original iron complex **17** resulting from approach of the tricarbonyliron fragment onto the face of the cyclohexadiene *anti* to the dihydroindole portion. Complete stereoselectivity was also observed for the Diels-Alder cycloaddition of **22** with 4-phenyl-1,2,4-triazoline-3,5-dione which afforded **28**.[5,22] *Exo* addition is assumed by analogy with the stereoselectivity of the $Fe(CO)_3$-recomplexation.

In summary we have demonstrated that tricarbonyliron-complexed 4a,9a-dihydro-9*H*-carbazoles are readily available either by chemoselective cyclizing dehydrogenation of the appropriate precursor complexes or by reduction of tricarbonyliron-complexed 4b,8a-dihydrocarbazol-3-ones. The corresponding free ligands resulting from oxidative demetallation exhibit useful reactivity, *e.g.* for stereoselective cycloadditions.

EXPERIMENTAL SECTION

All reactions were carried out using anhydrous and degassed solvents under an inert gas atmosphere. Flash chromatography: Baker silica gel (0.03-0.06 mm). Melting points: Reichert hot-stage. UV: Beckman 3600. IR: Bruker IFS-25 and Perkin-Elmer 1710. ^{1}H-NMR and ^{13}C-NMR: Bruker WP-200 and AM-300; internal standard: Tetramethylsilane or chloroform; coupling constants in Hz. Mass spectra: Finnigan MAT-312; ionization potential: 70 eV. Elemental analyses: Heraeus CHN-Rapid.

Tricarbonyl{(1-4-η)-4a,9a-dihydro-6-[6-tricarbonyl((2-5-η)cyclohexa-2,4-dienyl)iron-4-methoxy-2,3-dimethylphenylamino]-7,8-dimethyl-9*H*-carbazole}iron (11)

A solution of iron complex **9**[10b] (100 mg, 0.271 mmol) and *N*-ethyldiisopropylamine (52 µl, 0.298 mmol) in dichloromethane (4 ml) was added to a suspension of ferricenium hexafluorophosphate (99 mg, 0.298 mmol) in dichloromethane (4 ml). After 20 min of stirring at room temperature, diethyl ether (8 ml) was added and the reaction mixture was filtered through a short path of Celite. Removal of the solvent from the filtrate in vacuo and flash chromatography (diethyl ether/light petroleum, 1:3) of the residue on silica gel provided the dimeric complex **11** as light yellow crystals, yield: 78 mg (82%), m.p. 230°C (dec.). IR (KBr): ν = 2928, 2045, 1968, 1724, 1624, 1464, 1422, 1250, 1119, 1005, 622 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.56 (m), 2.03 (s, CH_3), 2.05 (s, 2 CH_3), 2.09 (s, CH_3), 2.12 (s, CH_3), 2.15-2.40 (m), 2.45 (s, CH_3), 2.66 (m), 2.95 (m), 3.03-3.32 (m), 3.32-3.45 (m), 3.45-3.60 (m), 3.78 (s, OCH_3), 3.82 (s, OCH_3), 3.80-4.20 (m), 4.46 (m), 5.05-5.50 (m), 6.27 (s), 6.38 (s), 6.55 (br s), 6.65 (s), 6.68 (s) (proton numbers could not be assigned completely). MS (210°C): *m/z* (%) = 704 (M^+, 88), 648 (5), 620 (22), 618 (34), 592 (5), 564 (17), 536 (58), 534 (74), 478 (47), 455 (24), 422 (47), 398 (25), 344 (6), 308 (13), 266 (23), 239 (17), 210 (12), 186 (39), 121 (100). HRMS: Calc. for $C_{35}H_{32}Fe_2N_2O_7$ (M^+): 704.0908, found: 704.0940.

Tricarbonyl[(1-4-η)-4a,9a-dihydro-5,6,7-trimethoxy-9*H*-carbazole]iron (14)

Ferricenium hexafluorophosphate (64 mg, 0.192 mmol) was added to a solution of complex **13**[9] (70 mg, 0.175 mmol) in CH_2Cl_2 (5 ml). The heterogeneous mixture was stirred for 2 h at room temperature. Removal of the solvent and flash chromatography (degassed EtOAc/light petroleum, 1:2) of the residue on degassed silica gel afforded complex **14** as light yellow crystals, yield: 15 mg (22%), m.p. 101°C (dec.). IR ($CHCl_3$): ν = 3385, 3013, 2937, 2050, 1981, 1609, 1484, 1473, 1436, 1420, 1382, 1343, 1278, 1203, 1197, 1120, 1040, 1003, 909 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 3.17 (m, 1 H), 3.66 (m, 1 H), 3.75 (s, 3 H), 3.76 (s, 3 H), 3.91 (dd, *J* = 10.8, 4.1, 1 H), 3.94 (s, 3 H), 4.32 (dd, *J* = 10.8, 3.5, 1 H), 5.40 (m, 2 H), 5.83 (s, 1 H).

Tricarbonyl[(1-4-η)-4a,9a-dihydro-6-hydroxy-7,8-dimethyl-9*H*-carbazole]iron (16)

Methanol (14.5 ml, 360 mmol) was added over a period of 20 min to a stirred suspension of complex **15**[10b] (1.15 g, 3.28 mmol) and sodium borohydride (1.24 g, 32.75 mmol) in tetrahydrofuran (29 ml) at 0°C. The reaction mixture was stirred for further 3 h at 0°C and subsequently quenched with a diluted aqueous solution of ammonium chloride (10 ml). The mixture was extracted three times with EtOAc and the combined organic layers were dried over magnesium sulfate. After removal of the solvent the residue was taken up in acetone and filtered through a short path (1 cm) of silica gel. The filtrate was evaporated, the residue was warmed (not completely dissolved!) in a small amount of ethyl acetate for a short period of time and subsequently diluted with a large amount (about twentyfold in volume) of light petroleum. For crystallization this solution was cooled to -28°C for 15 h. The precipitate was dried in high vacuum and gave complex **16** as colorless crystals, yield: 1.12 g (96%), m.p. 210°C (dec.). UV (MeOH): λ = 213, 225 (sh), 300 nm. IR (KBr): ν = 3400 (br), 2930, 2050, 1986, 1965, 1455, 1242, 1215, 1080, 618 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.97 (s, 3 H), 2.09 (s, 3 H), 3.23 (m, 1 H), 3.42 (m, 1 H), 3.79 (dd, *J* = 10.8, 4, 1 H), 4.32 (ddd, *J* = 10.8, 4, 0.9, 1 H), 5.38 (m, 2 H), 6.36 (s, 1 H). ^{1}H-NMR (300 MHz, DMSO-d_6): δ = 1.84 (s, 3 H), 1.92 (s, 3 H), 3.31 (m, 1 H), 3.56 (m, 1 H), 3.64 (dd, *J* = 10.7, 4.2, 1 H), 4.11 (dd, *J* = 10.7, 3.4, 1 H), 4.73 (br s, 1 H), 5.50 (m, 2 H), 6.33 (s, 1 H), 8.24 (br s, 1 H). ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 11.69 (q), 13.50 (q), 45.84 (d), 60.76 (d), 64.33 (d), 65.79 (d), 86.03 (d), 86.39 (d), 108.03 (d), 118.16 (s), 121.03 (s), 129.64 (s), 140.98 (s), 147.74 (s), 212.07 (s). MS (320°C): *m/z* (%) = 353 (M^+, 42), 325 (2), 323 (30), 297 (2), 269 (20), 267 (82), 210 (33), 190 (21), 188 (20), 86 (65), 79 (100). HRMS: Calc. for $C_{17}H_{15}FeNO_4$ (M^+): 353.0350, found: 353.0351.

Tricarbonyl[(1-4-η)-4a,9a-dihydro-6-methoxy-7,8,9-trimethyl-9*H*-carbazole]iron (17)

A solution of complex **16** (100 mg, 0.283 mmol) in tetrahydrofuran (4 ml) was added slowly to a suspension of sodium hydride (27 mg, 1.13 mmol) in tetrahydrofuran (4 ml). The heterogeneous reaction mixture was stirred at room temperature until the evolution of hydrogen diminished (about 10 to 20 min). Dimethyl sulfate (135 µl, 1.42 mmol) was added and the reaction mixture was stirred at room temperature for further 60 min. Removal of the solvent in vacuo and flash chromatography (degassed diethyl ether/light petroleum, 1:5) of the residue on degassed silica gel provided complex **17** as yellow crystals, yield: 85 mg (79%), m.p. 133°C. UV (MeOH): λ = 218, 268 (sh), 300 nm. IR (KBr): ν = 2930, 2040, 1988, 1976, 1965, 1957, 1465, 1457, 1252, 1113, 620 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 2.08 (s, 3 H), 2.12 (s, 3 H), 2.73 (s, 3 H), 3.41 (m, 2 H), 3.68 (ddd, *J* = 10.5, 4.1, 0.9, 1 H), 3.75 (s, 3 H), 3.97 (dd, *J* = 10.5, 4.1, 1 H), 5.33 (m, 2 H), 6.45 (s, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 12.04 (q), 15.48 (q), 43.13 (q), 44.95 (d), 56.29 (q), 62.77 (d), 63.19 (d), 72.87 (d), 85.73 (d), 85.99 (d), 104.24 (d), 123.78 (s), 125.43 (s), 133.62 (s), 144.94 (s), 153.17 (s), 211.59 (s). MS (80°C): *m/z* (%) = 381 (M^+, 100), 353 (1), 325 (16), 297 (51), 295 (98), 239 (38), 225 (33), 224 (22), 219 (27), 210 (23). HRMS: Calc. for $C_{19}H_{19}FeNO_4$ (M^+): 381.0663, found: 381.0664. Anal. Calc. for $C_{19}H_{19}FeNO_4$: C, 59.86; H, 5.02; N, 3.67. Found: C, 59.85; H, 5.07; N, 3.88.

X-ray crystal structure determination for 17

Formula: $C_{19}H_{19}FeNO_4$; M = 381.20; monoclinic; space group: $P2_1/c$; a = 10.439(1) Å, b = 13.948(8) Å, c = 12.315(1) Å; α = γ = 90°, β = 98.91(1)°; V = 1771.5(10) $Å^3$; Z = 4; ρ_{calc} = 1.429 g/cm^3; T = 200(2) K; μ = 0.874 mm^{-1}; $2\theta_{max}$ = 60°; reflections collected: 10928; independent reflections: 5170. The data were collected on a STOE STADI-4 diffractometer using graphite monochromated Mo-K_α radiation (λ = 0.71069 Å). The structure was solved by direct methods (SHELXS-86) and refined anisotropically by full-matrix least

squares based on all unique F^2 (SHELXL-93). R_1 = 3.62%; wR_2 = 9.19% [$I > 2\sigma(I)$]; maximal residual electron density: 0.287 e/Å^3. The hydrogen atoms at C15 and C16 are disordered.[15]
The program SCHAKAL-92 has been used for the graphical representation of the crystal structure.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **17**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Fe	856(1)	4326(1)	2320(1)	44(1)
C(1)	1571(2)	3489(2)	3709(2)	52(1)
C(2)	391(2)	3947(2)	3831(2)	61(1)
C(3)	398(2)	4946(2)	3721(2)	57(1)
C(4)	1578(2)	5347(1)	3513(1)	44(1)
C(5)	3079(2)	6265(1)	5719(1)	43(1)
C(6)	3236(2)	6402(2)	6850(1)	48(1)
C(7)	3341(2)	5631(2)	7580(2)	49(1)
C(8)	3277(2)	4690(2)	7172(2)	48(1)
N(9)	3069(2)	3670(1)	5453(1)	47(1)
C(10)	2848(2)	3897(1)	4257(2)	43(1)
C(11)	2852(2)	5002(1)	4147(1)	38(1)
C(12)	3062(2)	5332(1)	5329(1)	37(1)
C(13)	3176(2)	4550(1)	6029(2)	41(1)
O(4)	3285(2)	7312(1)	7320(1)	67(1)
C(14)	3115(4)	8100(2)	6610(2)	73(1)
C(15)	3491(2)	5835(2)	8804(2)	66(1)
C(16)	3234(3)	3832(2)	7926(2)	71(1)
C(20)	4101(3)	2956(2)	5742(3)	68(1)
C(17)	7(2)	5216(2)	1441(2)	55(1)
O(1)	-486(2)	5805(1)	894(2)	81(1)
C(18)	2317(2)	4302(2)	1744(2)	52(1)
O(2)	3262(2)	4319(1)	1390(2)	81(1)
C(19)	5(3)	3342(2)	1590(2)	66(1)
O(3)	-497(2)	2709(2)	1132(2)	103(1)

Tricarbonyl[(7-10-η)-6b,10a-dihydro-11-acetyl-5-hydroxy-11*H*-benzo[*a*]carbazole]iron (19)
A 20% solution of DIBAL in hexane (0.19 ml, 0.19 mmol) was added to a solution of complex **18**[9] (60 mg, 0.16 mmol) in tetrahydrofuran (5 ml) at -78°C. After 5 h of stirring at this temperature acetic anhydride (38 µl, 0.40 mmol) was added and the mixture was stirred for further 2 h at -78°C. Then methanol (0.5 ml) and water (2 ml) were added, the cooling bath was removed, and the mixture was stirred for further 30 min at room temperature. The reaction mixture was poured into a saturated aqueous solution of sodium bicarbonate (25 ml)

and extracted three times with ethyl acetate (20 ml). The combined organic layers were dried over magnesium sulfate. Evaporation of the solvent in vacuo and flash chromatography (diethyl ether/light petroleum, 5:1) of the residue on silica gel afforded complex **19** as colorless crystals, yield: 59 mg (88%). IR (KBr): ν = 2051, 1978, 1624, 1584, 1403, 1379, 1241, 1074, 764, 617, 565 cm^{-1}. ^{1}H-NMR (200 MHz, DMSO-d_6): δ = 2.24 (br s, 3 H), 3.57 (m, 1 H), 3.68 (m, 1 H), 3.99 (dd, *J* = 9.5, 4.7, 1 H), 4.90 (dd, *J* = 9.5, 3.1, 1 H), 5.45 (m, 2 H), 6.76 (s, 1 H), 7.35 (m, 2 H), 7.54 (m, 1 H), 8.06 (m, 1 H), 8.31 (s, 1 H). ^{13}C-NMR (75 MHz, DMSO-d_6): δ = 23.21 (q), 42.45 (d), 61.23 (d), 61.93 (d), 64.95 (d), 79.05 (d), 85.39 (d), 86.42 (d), 103.77 (d), 122.06 (d), 123.47 (d), 124.06 (s), 124.74 (d), 125.09 (s), 126.35 (s), 135.91 (s), 151.80 (s), 169.20 (s), 211.15 (s). MS (320°C): *m/z* (%) = 417 (M^+, 23), 375 (7), 361 (4), 333 (75), 296 (9), 290 (18), 277 (19), 255 (100), 235 (45), 214 (47), 204 (28).

3-Methoxy-1,2,9-trimethyl-9*H*-carbazole (4-Deoxy-9-methylcarbazomycin B) (21) and
4a,9a-Dihydro-6-methoxy-7,8,9-trimethyl-9*H*-carbazole (22)

A solution of complex **17** (250 mg, 0.656 mmol) in acetone (25 ml) was added to trimethylamine *N*-oxide dihydrate (437 mg, 3.94 mmol) and the heterogeneous reaction mixture was heated at reflux for 45 min. The cold mixture was filtered through a short path of Celite (which was subsequently washed with acetone) and the solvent was evaporated in vacuo from the combined filtrates. Flash chromatography (degassed diethyl ether/light petroleum, 1:3) of the residue on degassed silica gel afforded the carbazole **21** as the less polar fraction and the dihydrocarbazole **22** as the more polar fraction.

21: Colorless crystals, yield: 35 mg (22%), m.p. 153°C. IR (KBr): ν = 2942, 1622, 1600, 1578, 1495, 1463, 1441, 1408, 1280, 1211, 1145, 1106, 859, 761, 739, 724 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 2.72 (s, 3 H), 3.93 (s, 3 H), 4.04 (s, 3 H), 7.16 (ddd, *J* = 7.7, 6.8, 1.3, 1 H), 7.31 (br d, *J* = 7.7, 1 H), 7.38 (s, 1 H), 7.40 (m, 1 H), 7.97 (br d, *J* = 7.7, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 12.47 (q), 15.48 (q), 33.24 (q), 56.19 (q), 99.01 (d), 108.71 (d), 118.33 (d), 119.38 (d), 120.37 (s), 121.29 (s), 123.21 (s), 124.93 (d), 125.07 (s), 135.63 (s), 142.54 (s), 152.18 (s). MS (70°C): *m/z* (%) = 239 (M^+, 83%), 224 (100), 223 (64), 209 (61), 179 (12). HRMS: Calc. for $C_{16}H_{17}NO$ (M^+): 239.1310, found: 239.1309.

22: Colorless crystals, yield: 90 mg (57%). IR (KBr): ν = 3033, 2926, 2837, 1601, 1469, 1413, 1304, 1239, 1189, 1114, 1043, 844, 797, 713 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 2.12 (s, 3 H), 2.26 (s, 3 H), 2.80 (s, 3 H), 3.79 (s, 3 H), 4.00 (dd, *J* = 12, 4, 1 H), 4.16 (br d, *J* = 12, 1 H), 5.74 (m, 1 H), 5.89 (m, 2 H), 6.06 (dd, *J* = 10, 5, 1 H), 6.65 (s, 1 H). MS (40°C): *m/z* (%) = 241 (M^+, 100), 226 (84), 210 (16), 209 (11), 198 (9), 181 (8). HRMS: Calc. for $C_{16}H_{19}NO$ (M^+): 241.1467, found: 241.1467.

Tricarbonyl[(1-4-η)-4a,9a-dihydro-9-acetyl-6-methoxy-7,8-dimethyl-9*H*-carbazole]iron (23)

Pyridine (26 μl, 0.33 mmol) and acetic anhydride (77 μl, 0.82 mmol) were added to a solution of complex **10**[10b] (100 mg, 0.272 mmol) and *N,N*-dimethylaminopyridine (4 mg, 0.033 mmol) in dichloromethane (5 ml). The reaction mixture was stirred for 1 h at room temperature and diluted with ethyl acetate (25 ml). The organic layer was washed three times with diluted hydrochloric acid (20 ml) and two times with a saturated aqueous solution of NaCl. The organic layer was dried over magnesium sulfate and the solvent was removed. Flash chromatography (EtOAc/light petroleum, 1:1) of the residue on silica gel provided complex **23** as light yellow crystals, yield: 108 mg (97%), m.p. 210°C (dec.). IR (KBr): ν = 2926, 2048, 1964, 1668, 1599, 1467, 1422, 1400, 1379, 1301, 1285, 1238, 1121, 620 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 2.04 (br s, 3 H), 2.12 (s, 3 H), 2.19 (br s, 3 H), 3.35 (m, 1 H), 3.43 (m, 1 H), 3.79 (s, 3 H), 3.85 (m, 1 H), 4.78 (m, 1 H), 5.27 (m,

2 H), 6.50 (s, 1 H). ^{13}C-NMR and DEPT (75 MHz, $CDCl_3$): δ = 12.05 (CH_3), 18.71 (CH_3), 24.62 (CH_3), 43.00 (CH_3), 56.06 (CH), 60.69 (CH), 65.85 (CH), 77.54 (CH), 84.95 (CH), 86.43 (CH), 103.47 (CH), 124.93 (C), 132.13 (C), 136.77 (C), 155.83 (C), 210.64 (3 CO) (the signals for 1 C and 1 C=O are missing due to line broadening). MS (210°C): *m/z* (%) = 410 (M^++1, 70), 409 (M^+, 2), 382 (2), 354 (1), 353 (3), 326 (78), 325 (100), 323 (31), 297 (39), 282 (64), 269 (17), 267 (34), 248 (54), 247 (93), 232 (18), 227 (19), 217 (27), 212 (37), 206 (78). HRMS: Calc. for $C_{20}H_{19}FeNO_5$ (M^+): 409.0672, found: 409.0622. Anal. Calc. for $C_{20}H_{19}FeNO_5$: C, 58.70; H, 4.68; N, 3.42. Found: C, 58.54; H, 4.80; N, 3.62.

4a,9a-Dihydro-9-acetyl-6-methoxy-7,8-dimethyl-9*H*-carbazole (24)

Complex **23** (212 mg, 0.518 mmol) and trimethylamine *N*-oxide dihydrate (461 mg, 4.15 mmol) were stirred in acetone (15 ml) for 2 h at room temperature and for 1 h at reflux. After cooling the reaction mixture was diluted with diethyl ether (30 ml) and filtered through a short path of Celite. Removal of the solvent from the filtrate and flash chromatography (degassed diethyl ether/light petroleum, 5:1) of the residue on degassed silica gel afforded the dihydrocarbazole **24** as light yellow crystals, yield: 136 mg (97%), m.p. 84°C. IR (KBr): ν = 3042, 2935, 1664, 1600, 1467, 1426, 1379, 1312, 1284, 1203, 1120, 1019, 968, 750, 713 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 2.14 (s, 6 H), 2.25 (br s, 3 H), 3.79 (s, 3 H), 4.08 (m, 1 H), 5.30-5.65 (m, 2 H), 5.87 (m, 2 H), 6.10 (m, 1 H), 6.50 (br s, 1 H). MS (120°C): *m/z* (%) = 269 (M^+, 77), 267 (13), 238 (2), 227 (55), 226 (31), 225 (22), 224 (7), 212 (100), 211 (26), 210 (32), 196 (20), 195 (13), 194 (11), 182 (16), 180 (16), 168 (15), 167 (19). HRMS: Calc. for $C_{17}H_{19}NO_2$ (M^+): 269.1416, found: 269.1417.

9-Acetyl-6-methoxy-7,8-dimethyl-9*H*-carbazole (9-Acetyl-4-deoxycarbazomycin B) (25) and **N-Acetyl-4-methoxy-2,3-dimethyl-6-phenylaniline (26)**

10% Palladium on activated carbon (6 mg) was added to a solution of the dihydrocarbazole **24** (58 mg, 0.215 mmol) in degassed *p*-xylene (5.5 ml). The heterogeneous mixture was heated at reflux for 2.5 h. After cooling the reaction mixture was diluted with diethyl ether and filtered through a short path of Celite. Removal of the solvent in vacuo and flash chromatography (gradient elution: diethyl ether/light petroleum, from 1:2 to 5:1) of the residue on silica gel provided the carbazole **25** as the less polar fraction and the *N*-acetylaniline **26** as the more polar fraction.

25: Colorless crystals, yield: 37 mg (64%), m.p. 92°C. UV (MeOH): λ = 265, 295, 318 (sh) nm. IR ($CHCl_3$): ν = 3004, 2937, 2860, 1697, 1598, 1475, 1415, 1366, 1338, 1284, 1240, 1203, 1160, 1152, 1118, 1105, 1016, 910, 836 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 2.31 (s, 3 H), 2.37 (s, 3 H), 2.58 (s, 3 H), 3.95 (s, 3 H), 7.28 (br s, 1 H), 7.37 (m, 2 H), 7.87 (m, 1 H), 8.03 (m, 1 H). ^{13}C-NMR and DEPT (75 MHz, $CDCl_3$): δ = 12.23/12.56 (CH_3), 18.25/18.61 (CH_3), 26.60/27.09 (CH_3), 55.97/56.02 (CH_3), 96.92/98.71 (CH), 115.02 (CH), 119.33 (CH), 123.31 (CH), 122.12/124.44 (C), 125.82/126.06 (C), 126.66 (CH), 126.13/127.09 (C), 129.68/131.44 (C), 134.17/135.46 (C), 140.58 (C), 154.93/ 155.44 (C), 171.44/171.71 (C=O). MS (100°C): *m/z* (%) = 267 (M^+, 57), 225 (97), 224 (15), 210 (100), 209 (5), 201 (9), 194 (7), 181 (16), 180 (32), 167 (17). HRMS: Calc. for $C_{17}H_{17}NO_2$ (M^+): 267.1259, found: 267.1260.

26: Colorless crystals, yield: 12 mg (21%), m.p. 82°C. IR (KBr): ν = 3261 (br), 3000, 2931, 2857, 1657, 1599, 1572, 1525, 1466, 1402, 1375, 1338, 1289, 1231, 1195, 1159, 1109, 1080, 1016, 848, 769, 704 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.99 (s, 3 H), 2.20 (s, 3 H), 2.21 (s, 3 H), 3.81 (s, 3 H), 6.59 (br s, 1 H), 6.69 (s, 1 H), 7.34 (m, 5 H). MS (140°C): *m/z* (%) = 269 (M^+, 92), 254 (5), 227 (83), 212 (100), 196 (19), 182 (11), 168 (12), 167 (16). HRMS: Calc. for $C_{17}H_{19}NO_2$ (M^+): 269.1416, found: 269.1417.

[4a,9a-Dihydro-6-methoxy-7,8,9-trimethyl-9*H*-carbazole]-(1-4-η)-tricarbonyliron-(4b-8a-η)-tricarbonylchromium (27)

A solution of the iron complex **17** (100 mg, 0.262 mmol), tricarbonyl[η^6-naphthalene]chromium (90 mg, 0.341 mmol), and tetrahydrofuran (55 µl, 0.682 mmol) in di-*n*-butyl ether (5 ml) was heated for 1 h at 80°C and for 3.5 h at 100°C. After this time additional tricarbonyl[η^6-naphthalene]chromium (90 mg, 0.341 mmol) and tetrahydrofuran (55 µl, 0.682 mmol) were added and the solution was heated for further 3.5 h at 100°C. Removal of the solvent in vacuo and flash chromatography (degassed diethyl ether/light petroleum, 1:5) of the residue on degassed silica gel afforded the dinuclear complex **27** as orange crystals, yield: 36 mg (27%), m.p. 65°C (dec.). IR (KBr): ν = 2928, 2052, 1979, 1969 (sh), 1944, 1871, 1845, 1724, 1466, 1411, 1310, 1254, 1114, 1054, 744, 678, 618 cm^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 2.06 (s, 3 H), 2.18 (s, 3 H), 2.70 (s, 3 H), 3.27 (m, 2 H), 3.63 (dd, *J* = 10.9, 3.6, 1 H), 3.75 (s, 3 H), 3.89 (dd, *J* = 10.9, 3.6, 1 H), 5.03 (s, 1 H), 5.43 (m, 2 H). MS (220°C): *m/z* (%) = 517 (M^+, 4), 433 (7), 381 (45), 325 (20), 297 (47), 295 (100), 239 (69). HRMS: Calc. for $C_{22}H_{19}CrFeNO_7$ (M^+): 516.9916, found: 516.9915.

Tricarbonyl[(1-4-η)-4a,9a-dihydro-6-methoxy-7,8,9-trimethyl-9*H*-carbazole]iron (17)

A solution of the dihydrocarbazole **22** (80 mg, 0.331 mmol) in toluene (8 ml) was added to tricarbonyl[η^4-4-methoxybenzylideneacetone]iron (210 mg, 0.663 mmol). The reaction mixture was stirred for 2.5 h at room temperature and for 45 min at 60°C. Removal of the solvent in vacuo and flash chromatography (degassed diethyl ether/light petroleum, 1:5) of the residue on degassed silica gel provided complex **17** as yellow crystals, yield: 114 mg (90%); spectral data, see above.

Diels-Alder adduct 28

A solution of the dihydrocarbazole **22** (80 mg, 0.331 mmol) in dichloromethane (2 ml) was added over a period of 20 min *via* syringe pump to a solution of 4-phenyl-1,2,4-triazoline-3,5-dione (70 mg, 0.398 mmol) in acetone (6 ml) at 0°C. The reaction mixture was stirred for further 30 min at 0°C and the solvent was evaporated. Flash chromatography (diethyl ether/light petroleum, 1:1) of the residue on silica gel provided the Diels-Alder adduct **28** as colorless crystals, yield: 107 mg (78%), m.p. 210°C (dec.). IR (KBr): ν = 2923, 1775, 1718, 1600, 1503, 1468, 1407, 1255, 1131, 1114, 1079, 773 cm^{-1}. ^{1}H-NMR (200 MHz, CD_2Cl_2): δ = 2.06 (s, 3 H), 2.09 (s, 3 H), 2.86 (s, 3 H), 3.74 (s, 3 H), 3.98 (dd, *J* = 9.2, 3.8, 1 H), 4.33 (dd, *J* = 9.2, 3.2, 1 H), 5.13 (ddd, *J* = 5.5, 3.8, 1.6, 2 H), 6.20 (ddd, *J* = 7.5, 5.6, 1.4, 1 H), 6.40 (m, 1 H), 6.60 (s, 1 H), 7.44 (m, 5 H). ^{13}C-NMR and DEPT (75 MHz, $CDCl_3$): δ = 12.11 (CH_3), 15.58 (CH_3), 43.33 (CH_3), 46.09 (CH), 52.36 (CH_3), 53.00 (CH), 56.19 (CH), 67.94 (CH), 104.12 (CH), 123.55 (C), 125.58 (2 CH), 126.59 (C), 128.31 (CH), 129.14 (2 CH), 129.39 (CH), 129.98 (CH), 131.40 (C), 147.17 (C), 153.15 (C), 155.83 (C=O), 155.96 (C=O) (the signal of 1 C is missing due to overlapping). MS (160°C): *m/z* (%) = 416 (M^+, 1), 241 (2), 240 (2), 239 (2), 227 (9), 226 (4), 211 (2), 210 (2), 190 (14), 189 (100), 175 (6), 174 (37), 146 (14), 119 (10). HRMS: Calc. for $C_{24}H_{24}N_4O_3$ (M^+): 416.1848, found: 416.1844. Anal. Calc. for $C_{24}H_{24}N_4O_3$: C, 69.21; H, 5.81; N, 13.45. Found: C, 68.86; H, 5.83; N, 12.82.

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