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# Transition Metal-Diene Complexes in Organic Synthesis - 13.[1] Highly Chemo- and Stereoselective Oxidations of Tricarbonyliron-Cyclohexadiene Complexes: Synthesis of 4-Deoxycarbazomycin B

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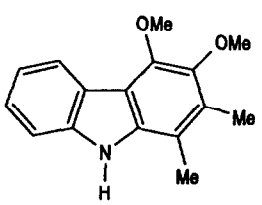
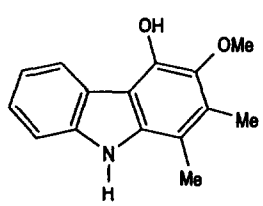
**Abstract:** Chemo- and stereoselectivity in oxidations of tricarbonyl[5-aryl-$\eta^4$-cyclohexa-1,3-diene]iron complexes is achieved by the choice of the oxidizing reagent. This procedure provides iron-complexed 4a,9a-dihydro-9*H*-carbazoles, 4b,8a-dihydrocarbazol-3-ones, and 4-deoxycarbazomycin B.

The carbazomycins A and B, isolated by Nakamura and co-workers in 1980 from microorganisms of the strain *Streptoverticillium ehimense* H 1051-MY 10, represent the first antibiotics with a carbazole skeleton [2-4] Moreover, they inhibit the growth of phytopathogenic fungi and have antibacterial and antiyeast activities The carbazomycins which biogenetically derive from tryptophan[5] exhibit an unusual congested substitution pattern It is tedious to achieve such an arrangement with four donor substituents at four adjacent carbon atoms of a carbazole ring system by classical synthetic routes [6] This fact and the useful biological activities induced several groups to develop synthetic strategies directed toward the total synthesis of the carbazomycins.[7-11]

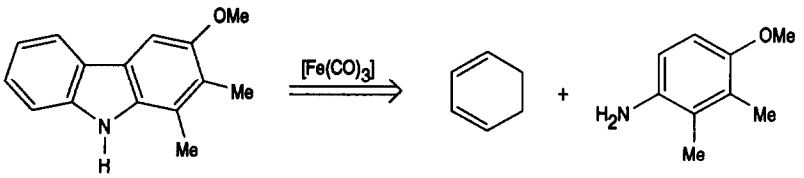



**carbazomycin A**




**carbazomycin B**

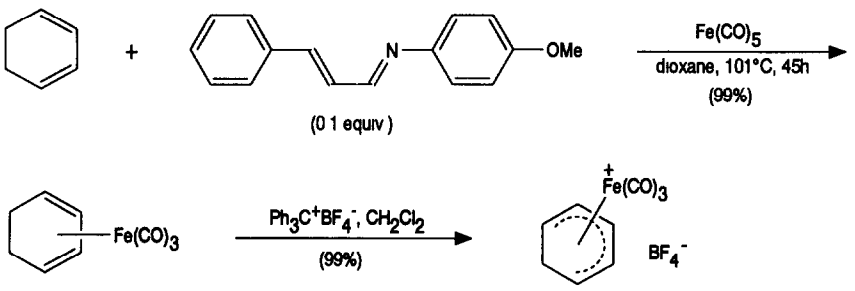
We envisaged a direct route to the carbazomycin antibiotics by a methodology of consecutive iron-induced C-C and C-N bond formation. 4-Deoxycarbazomycin B (**1**), a degradation product of carbazomycin B,[3,4] served as a model compound in order to develop a highly convergent synthesis of the carbazomycins using a sequence of electrophilic substitution of an arylamine by the tricarbonyl($\eta^5$-cyclohexadienylium)iron cation and subsequent oxidative cyclization[9] Tricarbonyl($\eta^4$-cyclohexa-1,3-diene)iron complexes have been shown to represent very useful intermediates for synthetic organic chemistry[12] Retrosynthetic analysis of 4-deoxycarbazomycin B based on the iron-mediated construction of the carbazole nucleus leads to 1,3-cyclohexadiene and 4-methoxy-2,3-dimethylaniline (**2**) as starting materials (Scheme 1)




**4-deoxycarbazomycin B** **2**

Scheme 1

1-Aza-1,3-butadiene-catalyzed $Fe(CO)_3$-complexation of 1,3-cyclohexadiene[13] and subsequent hydride abstraction with triphenylcarbenium tetrafluoroborate[14] provide easy access to large amounts of tricarbonyl($\eta^5$-cyclohexadienylium)iron tetrafluoroborate (**3**) in quantitative overall yield (Scheme 2)



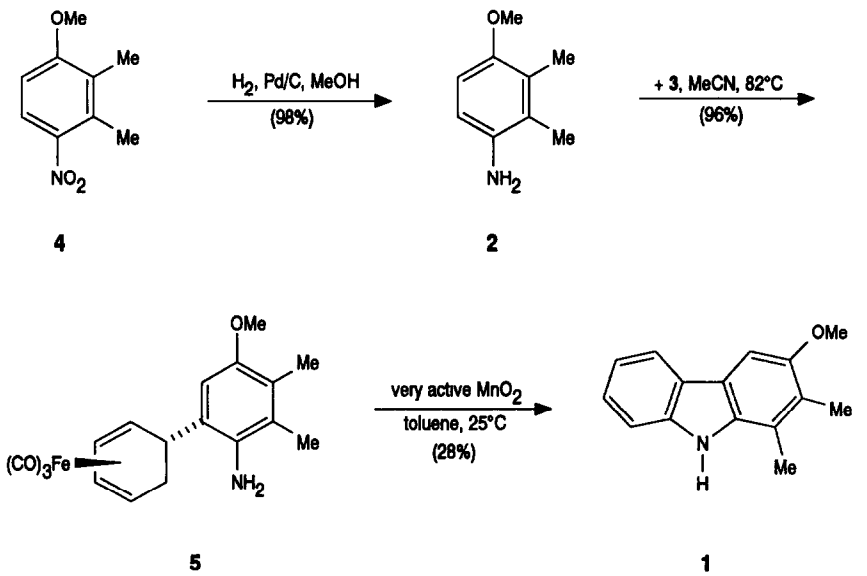

**3**

Scheme 2

The required arylamine **2** is obtained on a large scale by hydrogenation of the commercial nitroaryl derivative **4** (Scheme 3). Moreover, the nitro compound is easily prepared by *O*-methylation and subsequent nitration of 2,3-dimethylphenol. A described procedure,[15] however, where the arylamine **2** was obtained by hydrogenation of 2,3-dimethylnitrobenzene in sulfuric acid/methanol gave only a very low yield Electrophilic aromatic substitution of the arylamine **2** by the iron-complexed cation **3** in acetonitrile at reflux temperature provides regio- and stereoselectively the iron complex **5** in 96% yield The regiochemistry of the product is confirmed by the singlet for the aromatic proton at 6 59 ppm The *anti* orientation of the

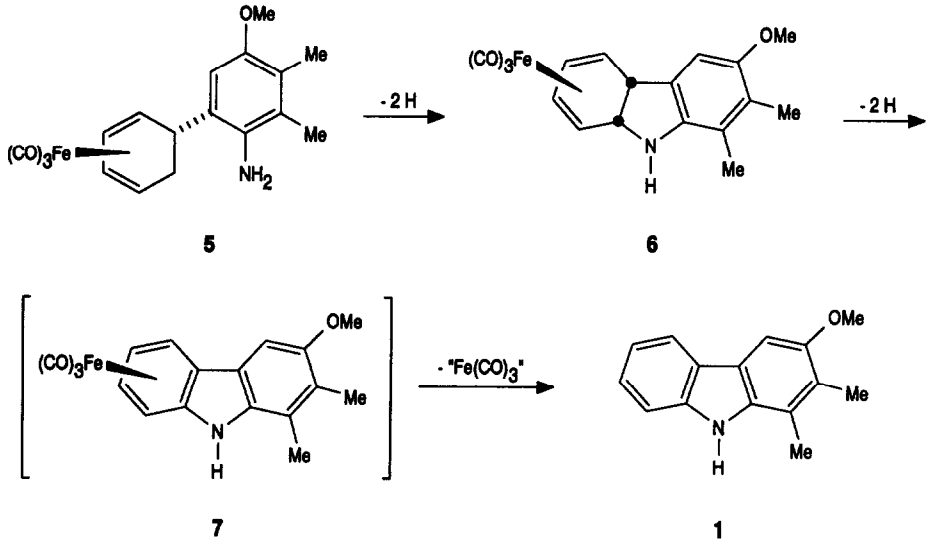
arylamine moiety is documented by the signal of the tertiary proton (3.43 ppm, dt, $J$ = 11, 4), which is shifted downfield because of the effect of magnetic anisotropy exhibited by the iron as observed in analogous cases [1] Moreover, the stereochemistry is supported by NOE experiments (see Experimental)

Oxidative cyclizations of tricarbonyliron-cyclohexadiene complexes with enols and alcohols by manganese dioxide at 80°C afforded already a broad range of annulated furan ring systems.[16] We recently reported on a direct access to oxygenated carbazoles by an iron-mediated arylamine cyclization with especially activated manganese dioxides at room temperature.[1] However, active γ-manganese dioxide,[17] successfully applied in the total synthesis of 3-methoxycarbazole,[1] provided 4-deoxycarbazomycin B in only 11% yield along with two by-products (see below) Oxidative cyclization of complex **5** using very active manganese dioxide[17] affords 4-deoxycarbazomycin B (**1**) in 28% yield after 4 h at room temperature (Scheme 3) The spectral data of the synthetic product obtained by this procedure are in full agreement with those reported by Nakamura and co-workers [3,4] The iron-mediated arylamine cyclization provides 4-deoxycarbazomycin B (**1**) in two steps and 27% overall yield based on cation **3**




Scheme 3

The direct one-pot transformation of the iron complex **5** to the carbazole **1** is believed to proceed via the sequence presented in Scheme 4. A selective cyclizing dehydrogenation of **5** leads to the 4a,9a-dihydro-9*H*-carbazole **6**, a potentially stable 18-electron complex. This process could be initiated by a single-electron transfer (SET) oxidation of the 18-electron complex **5** to an intermediate 17-electron radical cation [12c] A further aromatizing dehydrogenation of **6** affords the tricarbonyl($\eta^6$-arene)iron complex **7**, which represents a 20-electron complex and demetalates instantaneously to **1** by loss of the tricarbonyliron fragment




Scheme 4

The yield of the iron-mediated arylamine cyclization with concomitant aromatization to 4-deoxycarbazomycin B (1) using very active manganese dioxide is in the same range as previously described for the synthesis of 3-methoxycarbazole[1] with γ-manganese dioxide. The cyclizations of these iron complexes with different arylamine moieties seem to have different oxidation potentials We wanted to improve the overall yield of the sequence cyclization/aromatization/demetalation by the application of milder and therefore more selective oxidizing reagents The iron complex **5**, which is regio- and stereoselectively available almost quantitatively, appeared as an appropriate substrate for an optimization study. We investigated the selectivity of the oxidation of this complex depending on the oxidizing reagent and the reaction conditions This problem was of essential importance for further projected syntheses based on the iron-mediated construction of the carbazole nucleus. Moreover, it should be feasible to isolate the intermediate 4a,9a-dihydro-9*H*-carbazole by application of milder oxidizing reagents provided that the oxidation potential for the second (aromatizing) dehydrogenation is higher than for the first (cyclizing) dehydrogenation Transformation of this intermediate to 4-deoxycarbazomycin B would support the mechanism we proposed for the oxidative cyclization (Scheme 4)

The two by-products, which are obtained on cyclization of the iron complex **5** with the less active γ-manganese dioxide, represented the first indication for the possibility of selectivity control in these oxidations These by-products were shown to be the non-cyclized iminoquinone **8** and the 4b,8a-dihydrocarbazol-3-one **9** (Scheme 5) Structural assignments are based on $^1$H-NMR, $^{13}$C-NMR, and mass spectra (see Experimental), all of which indicate cleavage of the methyl ether and oxidation of the aromatic nucleus to an iminoquinone Complete assignments of the proton signals of the 4b,8a-dihydrocarbazol-3-one **9** was achieved by a $^1$H-$^1$H correlated COSY spectrum However, coincidence of the signals for the protons at C-8 and C-4b gives a multiplet at 3.49 ppm. The proton at C-8a is significantly shifted downfield (δ = 4 91 ppm) due to the deshielding caused by the C=N double bond The characteristic allylic coupling of $J$ = 1 9 Hz between the proton at C-4 and C-4b is not observed for the corresponding protons of the 4a,9a-dihydro-9*H*-carbazole

6 The structure of the iron-complexed 4b,8a-dihydrocarbazol-3-one has been unequivocally confirmed by an X-ray analysis of single crystals of **9** (Figure 1) [18] The crystal packing of **9** (Figure 2) differs significantly from that of the 4a,9a-dihydro-9*H*-carbazoles **6** (Figure 4), in a way that the iminoquinone rings which are arranged in parallel layers are shifted against each other in contrast to the aromatic rings of **6**

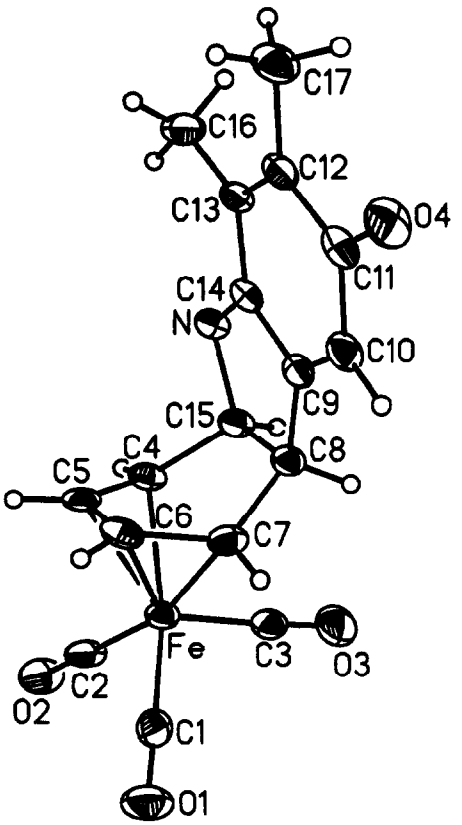



Figure 1 Crystal structure of **9**

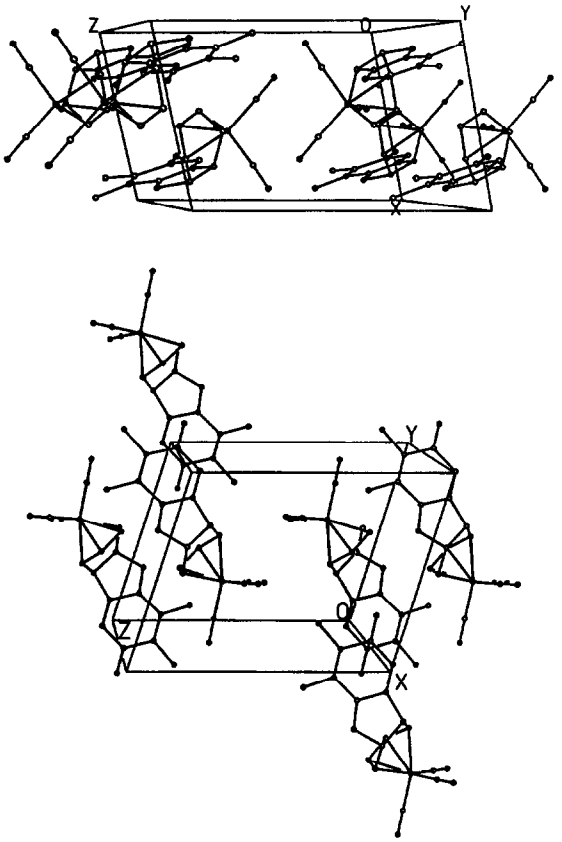
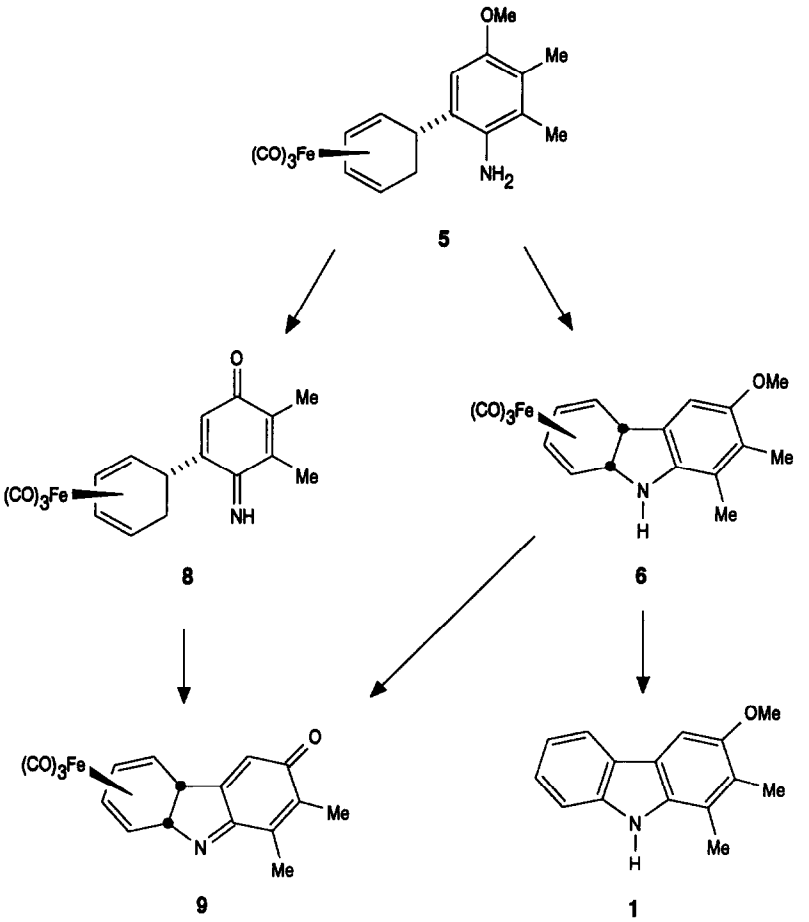



Figure 2 Crystal packing of **9**

In the course of the reaction to the 4b,8a-dihydrocarbazol-3-one **9** occurs an oxidation of the aromatic ring to the iminoquinone and no aromatization to a carbazole as observed in the generation of **1** The fact that the non-cyclized iminoquinone **8** is isolated as a by-product of this reaction suggests, that the oxidation of the aromatic ring is preceding the cyclizing dehydrogenation to **9** Therefore, it is postulated that the oxidation of iron complexes like **5** proceeds via two independent reaction pathways (Scheme 5) First, selective oxidation of the arylamine moiety to the non-cyclized iminoquinone **8** and subsequent stereoselective cyclization to the 4b,8a-dihydrocarbazol-3-one **9** Second, stereoselective cyclization to the 4a,9a-dihydro-9*H*-carbazole **6** followed by aromatization/demetalation to the carbazole **1** The possibility of a further pathway leading to the 4b,8a-dihydrocarbazol-3-one **9** by iminoquinone oxidation of the 4a,9a-dihydro-9*H*-carbazole **6** has to be considered as well




Scheme 5

In order to investigate the selectivity of the oxidation of complex **5** as a function of the oxidizing reagent we tested several manganese dioxides of different activity. Heterogeneous reaction conditions were deemed especially suitable for these oxidations because they enable an easy separation of reagent and product

An analysis of the results summarized in Table 1 shows that the activity of manganese dioxide prepared by a modified Attenburrow procedure[19] is too low for the projected transformations and because of long reaction times predominantly gives decomposition With active γ-manganese dioxide[17] the reaction follows both oxidation pathways almost to the same extent Whereas the oxidation with very active manganese dioxide[17] via cyclizing dehydrogenation, aromatization and demetalation directly leads to the carbazole **1** along with a trace of the cyclized iminoquinone **9** Chemoselective oxidation of complex **5** with commercial manganese dioxide[20] provides exclusively the non-cyclized iminoquinone **8** in 63% yield A further activation of the commercial manganese dioxide by azeotropic removal of water,[16b] sonochemical activation of $MnO_2$,[21] or application of $MnO_2$ supported on silica gel[22] gave no significant improvement in

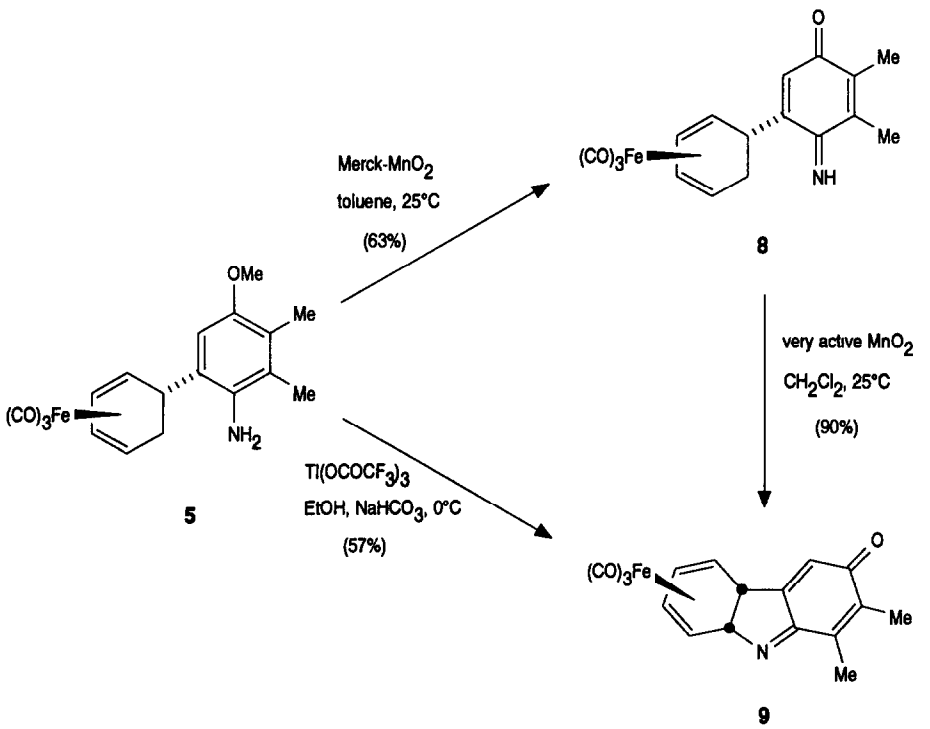
yield or selectivity The iminoquinone **8** is cyclized stereoselectively to the tricarbonyliron-complexed 4b,8a-dihydrocarbazol-3-one **9** with very active manganese dioxide (Scheme 6) This novel iron-mediated iminoquinone cyclization proceeds in 90% yield and therefore, is superior to the arylamine cyclization. Application of thallium trifluoroacetate as the oxidizing reagent[23] in this cyclization enables the direct transformation of complex **5** to the 4b,8a-dihydrocarbazol-3-one **9** in 57% yield.[24]

Table 1 Oxidations of iron complex **5** with manganese dioxides of different activity[a] and with thallium trifluoroacetate[b]

| | Att -$MnO_2$[19] | γ-$MnO_2$[17] | v a $MnO_2$[17] | $MnO_2$[20] | $Tl(OCOCF_3)_3$ |
|---|---|---|---|---|---|
| rct time | 4 days | 5h | 4h | 3h | 30 min |
| **1** | trace | 11 % | 28 % | - | - |
| **8** | 4 % | 10 % | - | 63 % | - |
| **9** | - | 5 % | trace | - | 57 % |

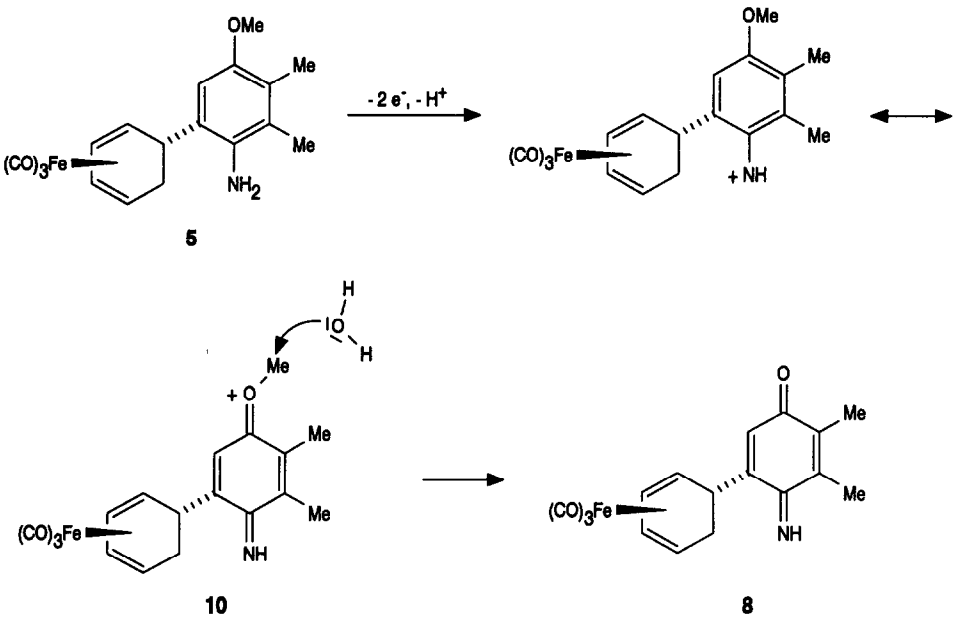
a) The oxidations with $MnO_2$ were performed in toluene at room temperature

b) Tl $(OCOCF_3)_3$ was applied in ethanol at 0°C with $NaHCO_3$ as buffer



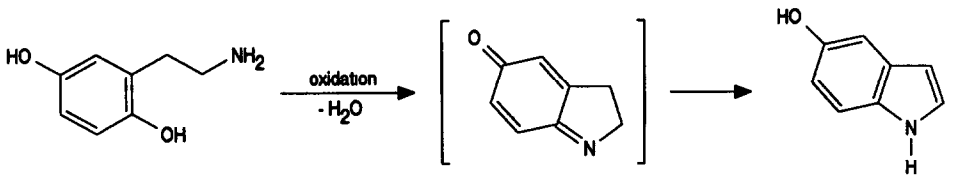

Scheme 6

Although there are previous examples of selective oxidations of functional groups in presence of a tricarbonyliron-diene moiety (e.g. osmylation,[25] Collin's oxidation,[12a] Sharpless epoxidation[26]), the oxidation of the iron complex **5** to the non-cyclized iminoquinone **8** represents the first example of chemoselective oxidation of an aromatic ring. The iron-mediated arylamine cyclization is believed to be initiated by a primary oxidative attack at the iron (SET oxidation) generating a 17-electron radical cation.[12c] We propose that the oxidation to the iminoquinone is achieved by a chemoselective attack at the arylamine moiety leading to the oxonium cation **10** (Scheme 7). Nucleophilic attack by water from the commercial manganese dioxide[20] then cleaves the methyl ether




Scheme 7

The tricarbonyliron-complexed 4b,8a-dihydrocarbazol-3-one **9** represents the first compound with a dihydrobenzene ring adjacent to an oxidized benzene ring The iron complex **9** which is obtained as yellow crystals is surprisingly stable in the air (decomposition above 198°C). This fact is very interesting from a theoretical point of view, since one would expect immediate isomerization of the free ligand with concomitant aromatization to the corresponding 3-hydroxycarbazole (a process which might alternatively considered an intramolecular redox reaction) In the context of melanin biogenesis Harley-Mason postulated, that the oxidation of 2,3-dihydroindoles leads to 2,3-dihydroindol-5-ones as intermediates [27] The 2,3-dihydroindol-5-ones are not stable and aromatize instantaneously by isomerization to the 5-hydroxyindoles (Scheme 8) An analogous isomerization of **9** to a 3-hydroxycarbazole would generate two complete aromatic 6$\pi$ systems Therefore, the driving force for such an aromatization process should be even much greater Complexation by the tricarbonyliron fragment appears to be responsible for the stabilization of the 4b,8a-dihydrocarbazol-3-one ring system Demetalation of the iron complex **9** provides indeed an easy access to the 3-hydroxycarbazole (see below)

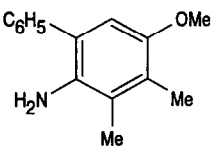



Scheme 8

The tricarbonyliron-complexed 4a,9a-dihydro-9*H*-carbazole **6** has been proposed as the crucial intermediate of the iron-mediated arylamine cyclization to 4-deoxycarbazomycin B (Scheme 4) We found that using appropriate reaction conditions the iron complex **6** can be isolated as a by-product along with the aromatized carbazole **1** (Table 2) Oxidation of complex **5** with ferric chloride supported on silica gel[28] mainly afforded the carbazole **1** (20% yield), but gave for the first time the 4a,9a-dihydro-9*H*-carbazole **6** as a by-product (15%) along with the 4b,8a-dihydrocarbazol-3-one **9** (6%) Dehydrogenation of **5** with palladium on charcoal at 80°C also provides **6** (11%), however aromatization to **1** (8%) cannot be avoided The main product of this reaction is the phenyl-substituted arylamine **11** (41%), which demonstrates that under these conditions direct aromatization of **5** is much faster than cyclizing dehydrogenation to **6**

Table 2 Results of cyclizing dehydrogenations of iron complex **5** to the 4a,9a-dihydro-9*H*-carbazole **6**

| product | $FeCl_3/SiO_2$ | 10 % Pd/C | $Cp_2Fe^+PF_6^-$ |
|---|---|---|---|
| **1** | 20 % | 8 % | - |
| **6** | 15 % | 11 % | 47 %* |
| **9** | 6 % | - | - |
| **11** | - | 41 % | - |




**11**

* In addition 42 % of starting material **5** were recovered under these conditions

We proposed that the cyclizing dehydrogenation to **6** is initiated by a SET oxidation [12c] Therefore, a chemoselective transformation of complex **5** to the 4a,9a-dihydro-9*H*-carbazole **6** should be possible by using SET oxidizing agents which are able to generate the postulated 17-electron intermediate under mild conditions Ferricenium hexafluorophosphate, a 17-electron complex with a known oxidation potential,[29] is easily prepared[30] and has already successfully been applied to the oxidation of transition metal complexes [31] These oxidations are very efficient since the stable 18-electron complex ferrocene is formed in this process Reaction of iron complex **5** with ferricenium hexafluorophosphate affords the iron-complexed 4a,9a-dihydro-9*H*-carbazole **6** by chemoselective oxidation (47% yield) along with 42% of recovered starting material More than 50% turnover in this reaction could not be achieved because 1 eq hexafluorophosphoric acid is formed which protonates the starting material The acid is removed after the oxidation by an external base (*N,N*-diisopropylethylamine) If the cyclization of complex **5** with the SET reagent is carried out in presence of this base a dimeric iron complex is formed (molecular ion at 704 *m/e*) in 82% yield The same dimeric iron complex is formed on oxidation of complex **5** with iodine in pyridine[32] at room temperature (54% yield) and with lead dioxide in toluene[16a] at 80°C (36% yield) Structural assignment of this product was not possible with certainty

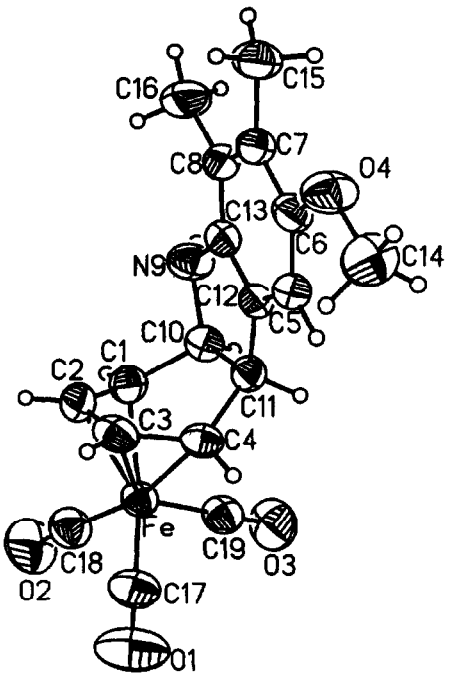



Figure 3 Crystal structure of **6**

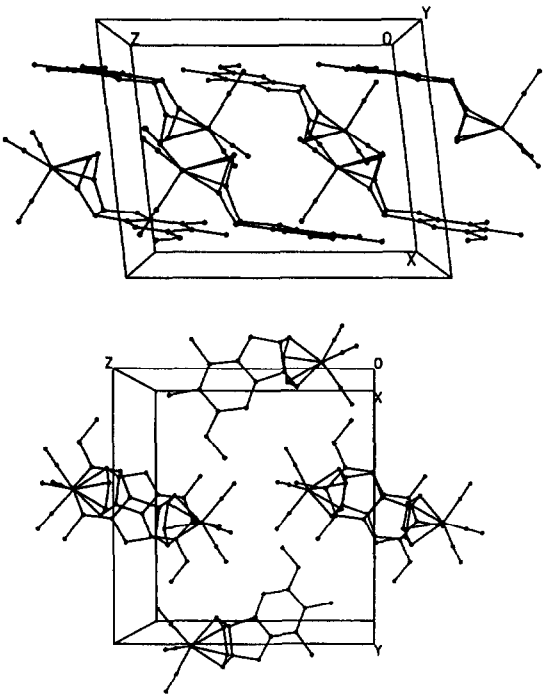
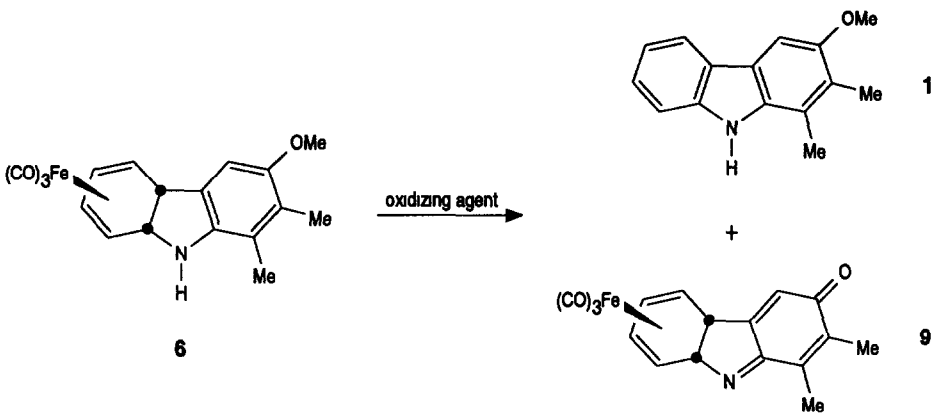



Figure 4 Crystal packing of **6**

The structure assignment of the 4a,9a-dihydro-9*H*-carbazole **6** is based on the $^{1}$H-NMR and $^{13}$C-NMR spectra (see Experimental) The proton signals have been assigned by a COSY spectrum The characteristic protons at C-4a and at C-9a both appear as a doublet of doublet at 3 84 ppm and at 4 32 ppm respectively with a vicinal coupling of $J$ = 11 Hz The aromatic proton at C-5 gives a singlet at 6 47 ppm The structure and stereochemistry (syn arrangement of both angular hydrogen atoms and the tricarbonyliron fragment) of complex **6** have additionally been confirmed by an X-ray crystal structure determination (Figure 3) [18] We found that single crystals of the tricarbonyliron-complexed 4a,9a-dihydro-9*H*-carbazole **6** exhibit optical anisotropism [9b] It represents columns which by rotation about the longitudinal axis appear red and yellow at orthogonal planes We believe that the crystal packing (Figure 4) is the reason for this interesting feature The crystal appears red when looking at the plane of the aromatic rings, which are arranged in parallel layers (YZ plane) Orthogonal to this direction (XZ plane) the crystals appear yellow The corresponding quinoid compound, the tricarbonyliron-complexed 4b,8a-dihydrocarbazol-3-one **9** has a different crystal packing mode (Figure 2) and does not exhibit an analogous feature. To our knowledge a similar optical anisotropy has not been observed yet with transition metal-diene complexes

This chemoselective cyclizing dehydrogenation provides direct access to the 4a,9a-dihydro-9*H*-carbazole ring system for the first time without additional annulated rings Generally, benzo-annulated bridgehead-dihydroheteroaromatic ring systems, such as the 3a,7a-dihydrobenzofurans,[16a] the 3a,7a-dihydroindoles,[33] the 3a,7a-dihydrobenzimidazoles,[34] and the 4a,9a-dihydro-9*H*-carbazoles,[9b,24,35] have been available so far exclusively by transition metal-mediated syntheses




Scheme 9

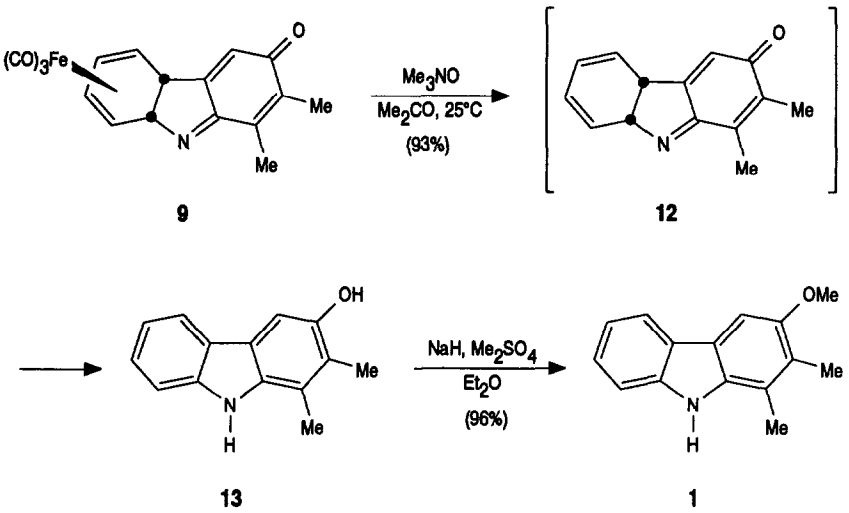
Table 3 Oxidation of the 4a,9a-dihydro-9*H*-carbazole **6**

| product | v a $MnO_2$[17] | $Cp_2Fe^+PF_6^-$ | $MnO_2$[20] |
|---|---|---|---|
| **1** | 74 % | 68 % | 8 % |
| **9** | 9 % | - | 73 % |

Treatment of the 4a,9a-dihydro-9*H*-carbazole **6** with very active manganese dioxide gives 4-deoxycarbazomycin B (**1**) in 74% yield along with the 4b,8a-dihydrocarbazol-3-one **9** (9% yield). This transformation is believed to proceed via the steps first, aromatization and second, demetalation The conversion of the 4a,9a-dihydrocarbazole **6** to the aromatized carbazole **1** supports the mechanism which was proposed for the iron-mediated arylamine cyclization (Scheme 4) Thus both oxidation pathways of the iron complex **5** which are presented in Scheme 5 can be realized in their two single steps The selectivity of these oxidations is controlled by the choice of the oxidant Complete chemoselectivity in the oxidation of **6** to **1** is achieved with ferricenium hexafluorophosphate It is suggested by this result that the aromatizing dehydrogenation, like the cyclizing dehydrogenation, is initiated by an SET process and takes place via the iron followed by a *syn*-stereospecific hydrogen shift and subsequent proton loss The attempt of a palladium-catalyzed dehydrogenation of **6** in an argon atmosphere (10% Pd/C, toluene, 72 h, 110°C) leads exclusively to recovery of the starting material Obviously, the sterical hindrance exhibited by the tricarbonyliron group prevents an approach of the two *syn* protons (4a-H and 9a-H) to the surface of the catalyst This outcome is considered a further indication that aromatization of **6** using very active manganese dioxide is initiated by oxidative attack at the iron Oxidation of the 4a,9a-dihydro-9*H*-carbazole **6** with commercial manganese dioxide[20] affords the 4b,8a-dihydrocarbazol-3-one **9** in 73% yield along with 8% of the aromatized carbazole **1**. Again with this type of manganese dioxide, containing water, a chemoselective oxidation of the aromatic ring to the iminoquinone moiety is achieved in the presence of the tricarbonyliron-diene unit This result furnishs evidence for the link between the iron-mediated arylamine cyclization and the iminoquinone cyclization as indicated in Scheme 5

The efficiency of the process cyclization/aromatization/demetalation in the course of the iron-mediated arylamine cyclization to 4-deoxycarbazomycin B (**1**) has been improved (three steps, 33% overall yield of **1** based on the iron complex salt **3**) by using in sequence the more selective ferricenium cation and then very active manganese dioxide as the oxidizing agents.

The much better yield of the iron-mediated iminoquinone cyclization prompted us to investigate its application to the synthesis of 4-deoxycarbazomycin B. In fact we can now take advantage of an aromatization process which is analogous to that predicted by Harley-Mason for the 2,3-dihydroindol-5-ones[27] Treatment of the 4b,8a-dihydrocarbazol-3-one **9** with trimethylamine *N*-oxide[36] at room temperature affords as expected directly the 3-hydroxycarbazole **13** in 93% yield (Scheme 10)




Scheme 10

In contrast to the tricarbonyliron-complexed 4b,8a-dihydrocarbazol-3-one **9**, which is highly stable in the air, immediate isomerization to the aromatized ring system **13** occurs at the stage of the free ligand **12** All attempts to trap the intermediate free ligand **12** in an intermolecular Diels-Alder cycloaddition by demetalation in presence of a highly reactive dienophile (dimethyl acetylenedicarboxylate and 4-phenyl-1,2,4-triazoline-3,5-dione[37]) have been unsuccessful Obviously the isomerization of **12** to **13** is much faster than the projected Diels-Alder reaction which indicates the high driving force for the aromatization process Treatment of the 3-hydroxycarbazole **13** with diazomethane gave only recovered starting material although, successful methylations of 1-hydroxy-,[38] 2-hydroxy-,[38] and 4-hydroxycarbazoles (*cf* the conversion of carbazomycin B to carbazomycin A)[2,4] using diazomethane have been described However, methylation of **13** to 4-deoxycarbazomycin B (**1**) is achieved in 96% yield with sodium hydride/dimethyl sulfate

The iron-mediated iminoquinone cyclization provides 4-deoxycarbazomycin B in four steps and 49% overall yield based on the iron complex salt **3** This result emphasize the superiority of the iminoquinone cyclization over the arylamine cyclization described above We are convinced that this cyclization mode represents a general and from a synthetic point of view very useful method for the synthesis of 3-oxygenated and 3,4-dioxygenated carbazole alkaloids Further applications are in progress

## EXPERIMENTAL SECTION

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 580 and 1710 (FTIR) $^1$H- and $^{13}$C-NMR Bruker WP-200, AM-300, and WM-400; internal standard tetramethylsilane or chloroform, coupling constants in Hz. Mass spectra: Finnigan MAT-312, ionization potential· 70 eV. Elemental analyses Heraeus CHN-Rapid All reactions were carried out by using dry and degassed solvents in an inert gas atmosphere

**4-Methoxy-2,3-dimethylaniline (2)**

To a solution of 2,3-dimethyl-4-nitroanisole (**4**) (5 0 g, 27 6 mmol) in methanol (130 ml) was added 10% palladium on activated carbon (0.5 g) The nitroaryl derivative **4** was hydrogenated by vigorous stirring of this mixture in an hydrogen atmosphere (1.1 atm) until no further hydrogen uptake was detected Filtration over a short path of Celite and subsequently over a short path of silica gel and evaporation of the solvent afforded the product which was dried in high vacuum A purification of the arylamine **2** was achieved by sublimation (95°C/0 05 mm) Yield 4 07 g (98%), colorless crystals, mp 67-68°C IR (KBr) ν 3437, 3359, 2996, 2959, 2834, 1632, 1483, 1462, 1256, 1222, 1105, 807 cm$^{-1}$; $^1$H-NMR (300 MHz, $CDCl_3$) δ 2 10 (s, 3 H), 2 17 (s, 3 H), 3 33 (br s, 2 H), 3.75 (s, 3 H), 6.53 (d, $J$ = 8.6, 1 H), 6.61 (d, $J$ = 8 6, 1 H); $^{13}$C-NMR (75 MHz, $CDCl_3$)· δ 12 2 (q), 13 4 (q), 56.5 (q), 109 7 (d), 113 0 (d), 123 3 (s), 126 1 (s), 138 5 (s), 151 3 (s), MS (25°C) *m/z* 151 ($M^+$, 75), 136 (100), 120 (3). Anal Calcd for $C_9H_{13}NO$ C, 71 49, H, 8 67, N, 9 26 Found. C, 71 41, H, 8.54, N, 9 35

**Tricarbonyl[(1-4-η)-5-(2-amino-5-methoxy-3,4-dimethylphenyl)-1,3-cyclohexadiene]iron (5)**

A solution of the complex salt **3** (2 57 g, 8.42 mmol) in dry acetonitrile (35 ml) was added over a period of 30 min under nitrogen to a refluxing solution of the arylamine **2** (2 80 g, 18 5 mmol) in dry acetonitrile (20 ml) After the addition was completed the reaction mixture was heated at reflux for further 45 min The solvent was removed in vacuo and the residue was taken up in diethyl ether and filtered through a short path of Celite. Evaporation of the solvent and flash chromatography (diethyl ether/light petroleum, 1:2) on silica gel provided 2 99 g (96%) of the iron complex **5** as light yellow crystals, mp 122°C. IR (KBr) ν 3445, 3403, 2930, 2039, 1957, 1622, 1483, 1461, 1424, 1336, 1276, 1233, 1119, 839, 625, 614, 568 cm$^{-1}$, $^1$H-NMR (300 MHz, $CDCl_3$) δ 1 61 (br d, $J$ = 15, 1 H), 2 08 (s, 3 H), 2 14 (s, 3 H), 2 40 (ddd, $J$ = 15, 11, 4, 1 H), 3 18 (m, 2 H), 3 33 (br s, 2 H), 3.43 (dt, $J$ = 11, 4, 1 H), 3 77 (s, 3 H), 5 52 (m, 2 H), 6 59 (s, 1 H), $^1$H-NMR NOE experiments (300 MHz, $CDCl_3$) 1. Irradiation at 2.40, observed NOE's 1 61, 3 18, 3 43, 2 irradiation at 3 43, observed NOE's 2 40, 3 18, 6.59, 3 irradiation at 5 52, observed NOE's 3.18, 6 59, $^{13}$C-NMR and DEPT (75 MHz, $CDCl_3$): δ 12 1 ($CH_3$), 13.6 ($CH_3$), 31 4 ($CH_2$), 39 4 (CH), 56.7 ($CH_3$), 60 3 (CH), 65.0 (CH), 84 9 (CH), 85 6 (CH), 108 2 (CH), 123 2 (C), 124 1 (C), 128 0 (C), 135 6 (C), 150 8 (C), 211 9 (CO), MS (80°C) *m/z* 369 ($M^+$, 27), 341 (3), 313 (24), 285 (61), 283 (75), 227 (12), 207 (100), 151 (33) Anal Calcd for $C_{18}H_{19}FeNO_4$ C, 58 56, H, 5 19, N, 3 79 Found C, 58 75, H, 5 20, N, 4 00

**4-Deoxycarbazomycin B (1)**

By arylamine cyclization of complex **5**

Very active manganese dioxide[17] (1 85 g) was added to a solution of the iron complex **5** (369 mg, 1 0 mmol) in dry toluene (25 ml) and the resulting mixture was stirred for 4 h at room temperature under

nitrogen. Filtration through a short path of Celite, removal of the solvent in vacuo and flash chromatography (diethyl ether/light petroleum, 1·4) of the residue on silica gel afforded 64 mg (28%) of 4-deoxycarbazomycin B (**1**) as colorless crystals, mp 130-132°C (lit.[3] mp 129-130°C, lit.[7a] mp 129-131°C, lit [10] mp 120-121°C). UV (EtOH): λ 216, 233, 251, 262, 293 (sh), 302, 334, 348 nm; IR (KBr) ν 3413, 2928, 1587, 1495, 1456, 1427, 1309, 1275, 1256, 1209, 1162, 1146, 1112, 1102, 765, 752, 733 $cm^{-1}$; $^1H$-NMR (200 MHz, $CDCl_3$) δ 2.34 (s, 3 H), 2.44 (s, 3 H), 3 94 (s, 3 H), 7 14-7 45 (m, 4 H), 7.76 (br s, 1 H), 7 99 (br d, $J$ = 8, 1 H); $^{13}C$-NMR (75 MHz, $CDCl_3$) δ 12.2 (q), 13 7 (q), 56 3 (q), 99 1 (d), 110 8 (d), 118.9 (d), 119 0 (s), 119 9 (d), 120 2 (s), 124 2 (s), 124.3 (s), 124 9 (d), 134 2 (s), 139 7 (s), 152 6 (s), MS (50°C) *m/z* 225 ($M^+$, 100), 210 (90), 194 (4), 182 (5), 180 (12), HRMS calcd for $C_{15}H_{15}NO$ ($M^+$) 225 1154, found: 225.1153

**Tricarbonyl[(1-4-η)-5-(6-imino-4,5-dimethylcyclohexa-1,4-dien-3-onyl)-1,3-cyclohexadiene]iron (8)**
Commercial manganese dioxide[20] (7 g) was added to a solution of the iron complex **5** (1 40 g, 3 79 mmol) in dry toluene (60 ml). The reaction mixture was stirred for 3 h at room temperature under nitrogen The mixture was filtered through a short path of Celite which was carefully washed with toluene several times Removal of the solvent from the combined filtrates in vacuo and subsequent recrystallization from ethyl acetate/diethyl ether/light petroleum (1 1 2) provided 848 mg (63%) of the non-cyclized iminoquinone **8** as yellow crystals, mp 172°C (dec.). UV (MeOH) λ 263 nm, IR (KBr) ν 3448, 2051, 1990, 1968, 1953, 1646, 1624, 1603, 1411, 1337, 1193, 1144, 864, 623, 615, 568 $cm^{-1}$, $^1H$-NMR (200 MHz, $CDCl_3$) δ 1 43 (d br, $J$ = 15, 1 H), 1.99 (br s, 3 H), 2 07 (br s, 3 H), 2 37 (ddd, $J$ = 15, 11 4, 3 7, 1 H), 3 03 (m, 1 H), 3 14 (m, 1 H), 3 88 (m, 1 H), 5 49 (m, 2 H), 6 49 (s, 1 H), 10 65 (br s) and 10 83 (br s, Σ 1 H), $^{13}C$-NMR and DEPT (75 MHz, $CDCl_3$) δ 12 0 ($CH_3$), 13 3 ($CH_3$), 32 6 ($CH_2$), 37.2 (CH), 60 4 (CH), 62 9 (CH), 84 8 (CH), 86 1 (CH), 126 9 (CH), 136 1 (C), 136 9 (C), 157 1 (C), 166 3 (C=N), 187 2 (C=O), 211 5 (CO), MS (90°C). *m/z* 353 ($M^+$, 4), 325 (14), 297 (37), 269 (52), 267 (100), 213 (11), 190 (44) Anal Calcd for $C_{17}H_{15}FeNO_4$ C, 57 82, H, 4 28, N, 3 97 Found C, 57 65, H, 4 27, N, 3 96

**Tricarbonyl[(5-8-η)-4b,8a-dihydro-1,2-dimethylcarbazol-3-one]iron (9)**
a) By cyclization of the iminoquinone **8**
Freshly prepared very active manganese dioxide[17] (1 24 g) was added to a solution of the non-cyclized iminoquinone **8** (248 mg, 0 70 mmol) in dry dichloromethane (33 ml) The heterogeneous reaction mixture was stirred for 105 min at room temperature under nitrogen Filtration through a short path of Celite (which was washed several times with dichloromethane), evaporation of the solvent from the combined filtrates in vacuo and flash chromatography (ethyl acetate/light petroleum, 1.3) of the residue on silica gel gave 220 mg (90%) of the iminoquinone **9** as yellow crystals, mp 198°C (dec.) UV (MeOH) λ 279 nm, IR (KBr) ν 2046, 1978, 1962, 1625, 621, 564 $cm^{-1}$, $^1H$-NMR (200 MHz, $CDCl_3$) δ 1 99 (s, 3 H), 2.19 (d, $J$ = 1, 3 H), 3 11 (m, 1 H), 3 49 (m, 2 H), 4 91 (dd, $J$ = 6 2, 4 4, 1 H), 5 41 (m, 2 H), 6 19 (d, $J$ = 1 9, 1 H), $^{13}C$-NMR and DEPT (75 MHz, $CDCl_3$) δ 12 2 ($CH_3$), 13 7 ($CH_3$), 45 2 (CH), 57 3 (CH), 59 2 (CH), 78 1 (CH), 85 3 (CH), 86 3 (CH), 122 4 (CH), 138 2 (C), 138 9 (C), 155 3 (C), 164 1 (C=N), 187 2 (C=O), 210 4 (CO), MS (100°C) *m/z* 351 ($M^+$, 13), 323 (98), 295 (38), 267 (100), 265 (28), 211 (6), 189 (50), 161 (14) Anal Calcd for $C_{17}H_{13}FeNO_4$ C, 58 15, H, 3 73, N, 3 99 Found C, 57 99, H, 3.83, N, 4 16

b) By cyclization of iron complex **5** with $Tl(OCOCF_3)_3$

The iron complex **5** (100 mg, 0.27 mmol) was dissolved under nitrogen in a mixture of dry ethanol (8 ml) and dry dichloromethane (1 ml) as the solvent. Sodium bicarbonate (75 mg, 0 89 mmol) and then thallium trifluoroacetate (310 mg, 0 57 mmol) were added and the reaction mixture was stirred for 30 min at 0°C under nitrogen. An excess of an aqueous solution of sodium carbonate and ethyl acetate were added, and the reaction mixture was stirred for 5 min, during which time the temperature rose to 25°C The reaction mixture was filtered through a short path of Celite which was subsequently washed with ethyl acetate The combined filtrates were washed with a saturated solution of sodium bicarbonate, then with water and dried over magnesium sulfate. Removal of the solvent in vacuo and flash chromatography (diethyl ether/light petroleum, 1 3) on silica gel afforded 54 mg (57%) of the iminoquinone **9** as yellow crystals, spectral data, see above

**X-ray crystal structure determination for 9**

Formula $C_{17}H_{13}FeNO_4$; crystal size 0 22 0 19 0 05 mm; triclinic, space group $P\bar{1}$, a = 7 697(4) Å, b = 9 305(5) Å, c = 11 467(6) Å, $\alpha$ = 107 92(4)°, $\beta$ = 100 53(4)°, $\gamma$ = 100 32(4)°, V = 743.5(7) Å$^3$, Z = 2, $\rho_{calcd}$ = 1 58 g/cm$^3$, T = 120 K, $\mu$ = 1 03 mm$^{-1}$, Mo-$K_\alpha$ radiation (graphite monochromator), scan range 3° < 2$\Theta$ < 52°, independent reflections 2390, observed 2073 [F > 4$\sigma$(F)], R = 0 053; $R_w$ = 0 051 [$w^{-1}$ = $\sigma^2$(F) + 0 000038 F$^2$]; maximal residual electron density 0 76 e/Å$^3$

Data collection and calculations were carried out using a Nicolet R3m/V four-circle diffractometer with a Micro VAX II computer and SHELXTL-PLUS software [18]

Table 4 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement factors (Å$^2$ x $10^3$)

| | | | | |
|---|---|---|---|---|
| Fe | 4235(1) | 6471(1) | 3167(1) | 21(1)* |
| N | 1096(5) | 3188(4) | -425(3) | 23(1)* |
| O(1) | 7281(5) | 7239(4) | 5401(3) | 43(2)* |
| O(2) | 4520(5) | 9765(4) | 3509(3) | 38(2)* |
| O(3) | 943(5) | 5827(4) | 4054(3) | 45(2)* |
| O(4) | 3017(5) | -2067(4) | -535(3) | 38(1)* |
| C(1) | 6063(7) | 6937(5) | 4533(5) | 27(2)* |
| C(2) | 4442(7) | 8482(5) | 3375(4) | 28(2)* |
| C(3) | 2268(7) | 6112(5) | 3736(4) | 29(2)* |
| C(4) | 2657(6) | 5699(5) | 1279(4) | 23(2)* |
| C(5) | 4542(7) | 5854(5) | 1351(4) | 26(2)* |
| C(6) | 5388(6) | 4976(5) | 1977(4) | 25(2)* |
| C(7) | 4223(6) | 4093(5) | 2477(4) | 25(2)* |
| C(8) | 2293(6) | 3167(5) | 1696(4) | 22(2)* |
| C(9) | 2265(6) | 1697(5) | 655(4) | 22(2)* |
| C(10) | 2741(6) | 395(5) | 668(5) | 26(2)* |
| C(11) | 2597(6) | -851(5) | -533(5) | 27(2)* |
| C(12) | 1936(6) | -610(5) | -1750(4) | 25(2)* |
| C(13) | 1436(6) | 699(5) | -1762(4) | 22(2)* |
| C(14) | 1558(6) | 1898(5) | -543(4) | 21(2)* |
| C(15) | 1409(6) | 4094(5) | 950(4) | 23(2)* |
| C(16) | 686(7) | 1001(6) | -2950(4) | 33(2)* |
| C(17) | 1887(7) | -1925(5) | -2934(5) | 34(2)* |

* Equivalent isotropic U defined as one third of the trace of the orthogonalized $U_{ij}$ tensor

Table 5 Bond lengths (Å)

| | | | |
|---|---|---|---|
| Fe–C(1) | 1.783 (5) | Fe–C(2) | 1 786 (5) |
| Fe–C(3) | 1 773 (6) | Fe–C(4) | 2 109 (4) |
| Fe–C(5) | 2 053 (5) | Fe–C(6) | 2 074 (5) |
| Fe–C(7) | 2 106 (4) | N–C(14) | 1 287 (6) |
| N–C(15) | 1 492 (5) | O(1)–C(1) | 1 158 (6) |
| O(2)–C(2) | 1 144 (6) | O(3)–C(3) | 1.159 (7) |
| O(4)–C(11) | 1 230 (6) | C(4)–C(5) | 1 416 (7) |
| C(4)–C(15) | 1 517 (6) | C(5)–C(6) | 1.410 (7) |
| C(6)–C(7) | 1 422 (7) | C(7)–C(8) | 1 527 (6) |
| C(8)–C(9) | 1.508 (6) | C(8)–C(15) | 1.546 (7) |
| C(9)–C(10) | 1 330 (7) | C(9)–C(14) | 1 463 (7) |
| C(10)–C(11) | 1 473 (6) | C(11)–C(12) | 1.493 (8) |
| C(12)–C(13) | 1 345 (7) | C(12)–C(17) | 1.511 (6) |
| C(13)–C(14) | 1 471 (6) | C(13)–C(16) | 1 508 (7) |

Table 6 Bond angles (°)

| | | | |
|---|---|---|---|
| C(1)–Fe–C(2) | 92.1(2) | C(1)–Fe–C(3) | 103.0(2) |
| C(2)–Fe–C(3) | 99 1(2) | C(1)–Fe–C(4) | 163 0(2) |
| C(2)–Fe–C(4) | 93.2(2) | C(3)–Fe–C(4) | 92 1(2) |
| C(1)–Fe–C(5) | 123.7(2) | C(2)–Fe–C(5) | 94 8(2) |
| C(3)–Fe–C(5) | 130 6(2) | C(4)–Fe–C(5) | 39 8(2) |
| C(1)–Fe–C(6) | 94.0(2) | C(2)–Fe–C(6) | 125 6(2) |
| C(3)–Fe–C(6) | 131 5(2) | C(4)–Fe–C(6) | 69 8(2) |
| C(5)–Fe–C(6) | 39.9(2) | C(1)–Fe–C(7) | 94 2(2) |
| C(2)–Fe–C(7) | 164 4(2) | C(3)–Fe–C(7) | 93 4(2) |
| C(4)–Fe–C(7) | 76 9(2) | C(5)–Fe–C(7) | 69 9(2) |
| C(6)–Fe–C(7) | 39.8(2) | C(14)–N–C(15) | 108 9(4) |
| Fe–C(1)–O(1) | 178 3(5) | Fe–C(2)–O(2) | 177 9(5) |
| Fe–C(3)–O(3) | 176 9(3) | Fe–C(4)–C(5) | 68 0(2) |
| Fe–C(4)–C(15) | 109 5(3) | C(5)–C(4)–C(15) | 119 5(4) |
| Fe–C(5)–C(4) | 72.2(3) | Fe–C(5)–C(6) | 70 8(3) |
| C(4)–C(5)–C(6) | 115 8(5) | Fe–C(6)–C(5) | 69 2(3) |
| Fe–C(6)–C(7) | 71 3(3) | C(5)–C(6)–C(7) | 114 7(4) |
| Fe–C(7)–C(6) | 68 9(3) | Fe–C(7)–C(8) | 108 1(3) |
| C(6)–C(7)–C(8) | 120 6(4) | C(7)–C(8)–C(9) | 112 7(4) |
| C(7)–C(8)–C(15) | 110 5(4) | C(9)–C(8)–C(15) | 102 5(4) |
| C(8)–C(9)–C(10) | 132 7(5) | C(8)–C(9)–C(14) | 106 6(4) |
| C(10)–C(9)–C(14) | 120 8(4) | C(9)–C(10)–C(11) | 120 0(5) |
| O(4)–C(11)–C(10) | 120 7(5) | O(4)–C(11)–C(12) | 120 6(4) |
| C(10)–C(11)–C(12) | 118 8(4) | C(11)–C(12)–C(13) | 121 2(4) |
| C(11)–C(12)–C(17) | 115 3(4) | C(13)–C(12)–C(17) | 123 6(5) |
| C(12)–C(13)–C(14) | 118 4(4) | C(12)–C(13)–C(16) | 124 3(4) |
| C(14)–C(13)–C(16) | 117.3(4) | N–C(14)–C(9) | 114 6(4) |
| N–C(14)–C(13) | 124 5(4) | C(9)–C(14)–C(13) | 120 9(4) |
| N–C(15)–C(4) | 109 6(4) | N–C(15)–C(8) | 107 2(4) |
| C(4)–C(15)–C(8) | 110 9(3) | | |

**4-Methoxy-2,3-dimethyl-6-phenylaniline (11)**

To a solution of the iron complex **5** (369 mg, 1.0 mmol) in dry toluene (5 ml) was added 10% palladium on activated carbon (401 mg) The reaction mixture was stirred at 80°C under nitrogen for 48 h. Filtration over a short path of Celite, evaporation of the solvent in vacuo and flash chromatography (diethyl ether/light petroleum, 1·3) of the residue on silica gel provided 3 fractions; fraction 1: 17 mg (8%) 4-deoxycarbazomycin B (**1**) (spetral data, see above); fraction 2. 92 mg (41%) phenylaniline **11**; fraction 3· 40 mg (11%) 4a,9a-dihydro-9*H*-carbazole **6** (spectral data, see below) The phenylaniline **11** and the starting material **5** have the same $R_f$ value. **11**: IR($CHCl_3$). ν 3008, 2940, 2839, 1613, 1476, 1462, 1417, 1338, 1280, 1131, 1105 $cm^{-1}$, $^1$H-NMR (200 MHz, $CDCl_3$) δ 2.17 (s, 3 H), 2 23 (s, 3 H), 3 45 (br s, 2 H), 3 77 (s, 3 H), 6 60 (s, 1 H), 7 30-7 50 (m, 5 H); MS (50°C) *m/z* 227 ($M^+$, 77), 212 (100), 197 (7), 183 (6), 181 (4), 179 (4), 169 (6), 168 (6), 167 (5), HRMS calcd for $C_{15}H_{17}NO$ ($M^+$)· 227.1310, found. 227 1310.

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

Ferricenium hexafluorophosphate (149 mg, 0.45 mmol) was added at room temperature to a stirred solution of the iron complex **5** (300 mg, 0.813 mmol) in dry dichloromethane (20 ml) After 30 min further ferricenium hexafluorophosphate (149 mg, 0.45 mmol) was added and the heterogeneous mixture was stirred for 1 h at room temperature under argon A solution of *N,N*-diisopropylethylamine (0 31 ml, 1 79 mmol) in dry dichloromethane (5 ml) was added over a period of 20 min and after further 15 min of stirring the solvent was removed in vacuo Flash chromatography (diethyl ether/light petroleum, 1·3) of the residue on degassed silica gel afforded the starting material **5** (126 mg, 42%) as the less polar fraction, the more polar fraction represents the 4a,9a-dihydro-9*H*-carbazole **6** (139 mg, 47%), yellow/red crystals, mp 164°C (dec ) IR (KBr) ν 3376, 3002, 2924, 2037, 1967, 1465, 1241, 1118, 619, 567 $cm^{-1}$; $^1$H-NMR (200 MHz, $CDCl_3$). δ 1 97 (s, 3 H), 2 08 (s, 3 H), 3 23 (m, 1 H), 3 49 (m, 1 H), 3.74 (s, 3 H), 3.84 (dd, *J* = 11, 4 4, 1 H), 4 32 (dd, *J* = 11, 3.4, 1 H), 5 38 (m, 2 H), 6 47 (s, 1 H); $^{13}$C-NMR and DEPT (75 MHz, $CDCl_3$)· δ 11 9 ($CH_3$), 13 7 ($CH_3$), 46 9 (CH), 56.6 ($CH_3$), 61 6 (CH), 62.9 (CH), 63 8 (CH), 85 7 (CH), 86 4 (CH), 105 0 (CH), 120.3 (C), 124.7 (C), 130 1 (C), 141 6 (C), 152 2 (C), 211.4 (CO); MS (60°C)· *m/z* 367 ($M^+$, 7), 342 (2), 325 (3), 323 (2), 311 (2), 283 (8), 281 (14), 269 (27), 254 (24), 229 (95), 228 (100), 214 (22), 212 (22) Anal Calcd for $C_{18}H_{17}FeNO_4$: C, 58 88, H, 4 67, N, 3 81 Found C, 58 54, H, 4 70; N, 3 96

**X-ray crystal structure determination for 6**

Formula· $C_{18}H_{18}FeNO_4$; crystal size: 0.33 · 0 21 0.18 mm, monoclinic; space group $P2_1/c$, a = 10 105(1) Å, b = 13 336(2) Å, c = 12.297(2) Å; α = γ = 90°, β = 96.27(1)°, V = 1647.3(4) $Å^3$; Z = 4, $\rho_{calcd}$ = 1 485 $g/cm^3$; T = 293 K; μ = 0.93 $mm^{-1}$; Mo-$K_\alpha$ radiation (graphite monochromator); scan range· 3° < 2Θ < 45°, independent reflections 2915, observed· 2572 [F > 4σ(F)], R = 0 037, $R_w$ = 0 045 [$w^{-1} = \sigma^2(F) + 0\ 003\ F^2$]; maximal residual electron density 0 50 e/$Å^3$

Data collection and calculations were carried out using a Nicolet R3m/V four-circle diffractometer with a Micro VAX II computer and SHELXTL-PLUS software.[18]

Table 7. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement factors (Å$^2$ x $10^3$)

| | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| Fe | 4141(1) | 9342(1) | 2157(1) | 40(1)* |
| O(1) | 5359(3) | 10908(2) | 932(2) | 92(1)* |
| O(2) | 5736(3) | 7740(2) | 1337(2) | 93(1)* |
| O(3) | 1729(2) | 8983(2) | 690(2) | 84(1)* |
| O(4) | 1277(2) | 12382(1) | 6579(1) | 62(1)* |
| C(1) | 3588(2) | 8477(2) | 3467(2) | 46(1)* |
| C(2) | 4725(3) | 9082(2) | 3790(2) | 51(1)* |
| C(3) | 4555(2) | 10111(2) | 3611(2) | 48(1)* |
| C(4) | 3260(2) | 10395(2) | 3139(2) | 40(1)* |
| C(5) | 1649(2) | 11293(2) | 5046(2) | 40(1)* |
| C(6) | 1475(2) | 11443(2) | 6139(2) | 44(1)* |
| C(7) | 1484(2) | 10641(2) | 6888(2) | 45(1)* |
| C(8) | 1664(2) | 9663(2) | 6514(2) | 45(1)* |
| N(9) | 2092(3) | 8610(2) | 4905(2) | 52(1)* |
| C(10) | 2223(2) | 8798(2) | 3736(2) | 42(1)* |
| C(11) | 2044(2) | 9948(2) | 3568(2) | 38(1)* |
| C(12) | 1832(2) | 10318(2) | 4690(2) | 37(1)* |
| C(13) | 1840(2) | 9524(2) | 5412(2) | 40(1)* |
| C(14) | 1270(4) | 13214(2) | 5879(3) | 67(1)* |
| C(15) | 1291(3) | 10858(3) | 8056(2) | 60(1)* |
| C(16) | 1652(3) | 8754(2) | 7239(3) | 65(1)* |
| C(17) | 4895(3) | 10289(2) | 1410(2) | 55(1)* |
| C(18) | 5141(3) | 8366(2) | 1668(2) | 58(1)* |
| C(19) | 2666(3) | 9125(2) | 1269(2) | 50(1)* |

* Equivalent isotropic U defined as one third of the trace of the orthogonalized $U_{ij}$ tensor

Table 8. Bond lengths (Å)

| | | | |
|---|---|---|---|
| Fe-C(1) | 2 106 (3) | Fe-C(2) | 2 060 (3) |
| Fe-C(3) | 2 063 (2) | Fe-C(4) | 2 111 (2) |
| Fe-C(17) | 1.780 (3) | Fe-C(18) | 1 791 (3) |
| Fe-C(19) | 1 773 (3) | O(1)-C(17) | 1.143 (4) |
| O(2)-C(18) | 1.131 (4) | O(3)-C(19) | 1.136 (3) |
| O(4)-C(6) | 1 387 (3) | O(4)-C(14) | 1 404 (3) |
| C(1)-C(2) | 1.426 (4) | C(1)-C(10) | 1.515 (3) |
| C(2)-C(3) | 1.398 (4) | C(3)-C(4) | 1 423 (3) |
| C(4)-C(11) | 1 512 (3) | C(5)-C(6) | 1 390 (3) |
| C(5)-C(12) | 1 391 (3) | C(6)-C(7) | 1 410 (3) |
| C(7)-C(8) | 1 401 (4) | C(7)-C(15) | 1.499 (4) |
| C(8)-C(13) | 1 399 (3) | C(8)-C(16) | 1.506 (4) |
| N(9)-C(10) | 1 480 (3) | N(9)-C(13) | 1 405 (3) |
| C(10)-C(11) | 1 555 (3) | C(11)-C(12) | 1 503 (3) |
| C(12)-C(13) | 1.380 (3) | | |

Table 9. Bond angles (°)

| | | | |
|---|---|---|---|
| C(1)-Fe-C(2) | 40.0(1) | C(1)-Fe-C(3) | 69.9(1) |
| C(2)-Fe-C(3) | 39.6(1) | C(1)-Fe-C(4) | 76.3(1) |
| C(2)-Fe-C(4) | 69.4(1) | C(3)-Fe-C(4) | 39.8(1) |
| C(1)-Fe-C(17) | 161.4(1) | C(2)-Fe-C(17) | 122.0(1) |
| C(3)-Fe-C(17) | 92.1(1) | C(4)-Fe-C(17) | 93 1(1) |
| C(1)-Fe-C(18) | 93.7(1) | C(2)-Fe-C(18) | 95 3(1) |
| C(3)-Fe-C(18) | 125.7(1) | C(4)-Fe-C(18) | 164 5(1) |
| C(17)-Fe-C(18) | 93.1(1) | C(1)-Fe-C(19) | 96 1(1) |
| C(2)-Fe-C(19) | 134.8(1) | C(3)-Fe-C(19) | 133 8(1) |
| C(4)-Fe-C(19) | 94.7(1) | C(17)-Fe-C(19) | 100.1(1) |
| C(18)-Fe-C(19) | 98.1(1) | C(6)-O(4)-C(14) | 117 7(2) |
| Fe-C(1)-C(2) | 68.3(1) | Fe-C(1)-C(10) | 109 6(2) |
| C(2)-C(1)-C(10) | 120 3(2) | Fe-C(2)-C(1) | 71.7(1) |
| Fe-C(2)-C(3) | 70.3(1) | C(1)-C(2)-C(3) | 115 5(2) |
| Fe-C(3)-C(2) | 70.1(1) | Fe-C(3)-C(4) | 71.9(1) |
| C(2)-C(3)-C(4) | 114.7(2) | Fe-C(4)-C(3) | 68.3(1) |
| Fe-C(4)-C(11) | 110 3(2) | C(3)-C(4)-C(11) | 119 9(2) |
| C(6)-C(5)-C(12) | 118 3(2) | O(4)-C(6)-C(5) | 123 1(2) |
| O(4)-C(6)-C(7) | 114.9(2) | C(5)-C(6)-C(7) | 122 0(2) |
| C(6)-C(7)-C(8) | 119.0(2) | C(6)-C(7)-C(15) | 119 1(2) |
| C(8)-C(7)-C(15) | 121.9(2) | C(7)-C(8)-C(13) | 118 4(2) |
| C(7)-C(8)-C(16) | 123.1(2) | C(13)-C(8)-C(16) | 118 5(2) |
| C(10)-N(9)-C(13) | 108 9(2) | C(1)-C(10)-N(9) | 110.1(2) |
| C(1)-C(10)-C(11) | 110 2(2) | N(9)-C(10)-C(11) | 105.9(2) |
| C(4)-C(11)-C(10) | 110 4(2) | C(4)-C(11)-C(12) | 113.2(2) |
| C(10)-C(11)-C(12) | 103 2(2) | C(5)-C(12)-C(11) | 129 2(2) |
| C(5)-C(12)-C(13) | 120.5(2) | C(11)-C(12)-C(13) | 110.3(2) |
| C(8)-C(13)-N(9) | 126.4(2) | C(8)-C(13)-C(12) | 121 9(2) |
| N(9)-C(13)-C(12) | 111.7(2) | Fe-C(17)-O(1) | 178 8(3) |
| Fe-C(18)-O(2) | 177 7(3) | Fe-C(19)-O(3) | 179 2(3) |

**Tricarbonyl[(5-8-η)-4b,8a-dihydro-1,2-dimethylcarbazol-3-one]iron (9)**

By oxidation of **6** with commercial $MnO_2$

Commercial manganese dioxide[20] (425 mg) was added to a solution of the 4a,9a-dihydro-9*H*-carbazole **6** (85 mg, 0 231 mmol) in dry toluene (7 ml) and the heterogeneous reaction mixture was stirred at room temperature under argon for 1 h Filtration through a short path of Celite (which was subsequently washed with ethyl acetate), removal of the solvent from the combined filtrates in vacuo and flash chromatography (ethyl acetate/light petroleum, 1 3) gave 4 mg (8%) of 4-deoxycarbazomycin B (**1**) as the less polar fraction (colorless crystals) and 59 mg (73%) of the iminoquinone **9** as the more polar fraction (yellow crystals).

**4-Deoxycarbazomycin B (1)**

By oxidation of **6** with very active $MnO_2$

Very active manganese dioxide[17] (450 mg) was added to a solution of the 4a,9a-dihydro-9*H*-carbazole **6** (90 mg, 0 245 mmol) in dry toluene (7.5 ml) and the reaction mixture was stirred at room temperature under argon for 4 5 h The heterogeneous mixture was filtered through a short path of Celite which was carefully washed with ethyl acetate. The combined filtrates were taken to dryness by removal of the solvent in vacuo. Flash chromatography (diethyl ether/light petroleum, 1 3) of the residue on silica gel provided 41 mg (74%) of 4-deoxycarbazomycin B (**1**) as colorless crystals and 8 mg (9%) of the iminoquinone **9** as yellow crystals

**4-Deoxycarbazomycin B (1)**

By oxidation of **6** with $Cp_2Fe^+PF_6^-$

Ferricenium hexafluorophosphate (71 mg, 0.216 mmol) was added to a solution of the 4a,9a-dihydro-9*H*-carbazole **6** (72 mg, 0.196 mol) in dry dichloromethane (4 ml) and the heterogeneous reaction mixture was stirred at room temperature under argon for 20 min A solution of *N,N*-diisopropylethylamine (37 µl, 0 216 mmol) in dry dichloromethane (0.5 ml) was added over a period of 10 min, further ferricenium hexafluorophosphate (71 mg, 0.216 mmol) was added and after 20 min of stirring *N,N*-diisopropylethylamine (37 µl, 0 216 mmol) in dry dichloromethane (0.5 ml) was again added over a period of 10 min The reaction mixture was diluted with diethyl ether, filtered through a short path of Celite and the solvent was evaporated in vacuo Flash chromatography (diethyl ether/light petroleum, 1:3) of the residue on silica gel gave 30 mg (68%) of 4-deoxycarbazomycin B (**1**) as colorless crystals.

**3-Hydroxy-1,2-dimethyl-9*H*-carbazole (13)**

A solution of the iminoquinone **9** (50 mg, 0.14 mmol) in dist acetone (8 ml) was added to trimethylamine *N*-oxide dihydrate (125 mg, 1.12 mmol) and the heterogeneous mixture was stirred at room temperature under nitrogen for 5 h. Filtration through a short path of Celite, removal of the solvent in vacuo and flash chromatography (diethyl ether/light petroleum, 1 2) of the residue on silica gel afforded 28 mg (93%) of the 3-hydroxycarbazole **13** as colorless crystals, mp 202°C UV (MeOH) λ 215, 232, 252, 263, 292 (sh), 300, 338, 350 nm, IR (KBr). ν 3433, 3310 (br), 2926, 1594, 1504, 1467, 1436, 1315, 1299, 1266, 1247, 1180, 1160, 1060, 848, 767, 751, 733 $cm^{-1}$; $^1$H-NMR (300 MHz, $CD_3OD$) δ 2 35 (s, 3 H), 2 50 (s, 3 H), 7 08 (ddd, *J* = 7 9, 7.2, 1 0, 1 H), 7 30 (ddd, *J* = 8 2, 7 2, 1 0, 1 H), 7 33 (s, 1 H), 7 43 (dd, *J* = 8 2, 1 0, 1 H), 7 90 (dd, *J* = 7 9, 1 0, 1 H), $^1$H-NMR (200 MHz, $CD_3SOCD_3$): δ 2 23 (s, 3 H), 2 43 (s, 3 H), 7 03 (dt, *J* = 1 0, 7 6, 1 H), 7 27 (dt, *J* = 1 0, 7.6, 1 H), 7 28 (s, 1 H), 7.41 (d, *J* = 7 6, 1 H), 7 88 (d, *J* = 7 6, 1 H), 8 82 (s, 1 H), 10 70 (s, 1 H), $^{13}$C-NMR and DEPT (75 MHz, $CD_3OD$): δ 12.4 ($CH_3$), 13 8 ($CH_3$), 103 0 (CH), 111.6 (CH), 118 8 (CH), 120 0 (C), 120 3 (CH), 121 5 (C), 123 2 (C), 124 6 (C), 125 5 (CH), 135 7 (C), 141.8 (C), 149.7 (C), MS (110°C) *m/z* 211 ($M^+$, 100), 210 (31), 195 (11), 179 (4), 166 (6), 111 (10), HRMS calcd for $C_{14}H_{13}NO$ ($M^+$). 211.0997, found 211 0998. Anal Calcd for $C_{14}H_{13}NO$ C, 79 59, H, 6 20; N, 6 63 Found C, 79 25, H, 6 18; N, 7 12

**4-Deoxycarbazomycin B (1)**

By alkylation of the 3-hydroxycarbazole **13**

A solution of the 3-hydroxycarbazole **13** (60 mg, 0.28 mmol) in dry diethyl ether (5 ml) was added to a suspension of sodium hydride (10 mg, 0 42 mmol) in dry diethyl ether (10 ml) under nitrogen The heterogeneous mixture was stirred at room temperature until the hydrogen evolution diminished (about 15 min) Dimethyl sulfate (78 mg, 59 µl, 0 62 mmol) was added and the reaction mixture was stirred at room temperature under nitrogen for further 6 h The reaction mixture was poured into a solution of ammonium chloride (30 ml) and extracted 3 times with diethyl ether (30 ml) The combined extracts were dried over magnesium sulfate Removal of the solvent in vacuo and flash chromatography (diethyl ether/light petroleum, 1.2) of the residue on silica gel provided 61 mg (96%) of 4-deoxycarbazomycin B (**1**) as colorless crystals; spectral data, see above

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