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# Regio- and Stereoselectivity of Electrophilic Substitutions of Arylamines by Tricarbonyliron-Complexed Cyclohexadienylium Cations and Oxidative Cyclizations to Carbazoles

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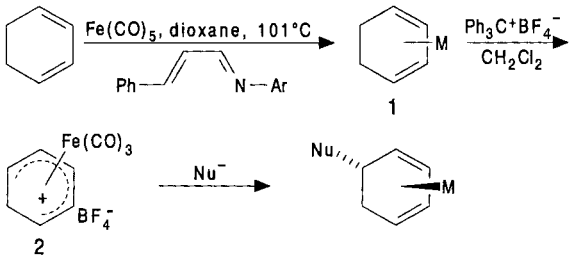
Electrophilic substitutions of donor-substituted arylamines using tricarbonyliron-complexed cyclohexadienylium cations lead regio- and stereoselectively to the corresponding tricarbonylcyclohexadieneiron complexes. The C–C bond formations occur regioselectively in the *ortho* position with respect to the amino group with arylamines containing a substituent in the *para* position. The initially formed *N*-alkylated arylamine (kinetic product) is shown to rearrange in an intermolecular process to the *C*-alkylated arylamine (thermodynamic product). The reported oxidative cyclization to 3-methylcarbazole yields large amounts of the demetalated ligand. However, oxidative cyclization to 3-methoxycarbazole is possible under mild reaction conditions (room temperature) by using especially activated manganese dioxides.

Tricarbonyl($\eta^5$-cyclohexadienylium)iron tetrafluoroborate (**2**) is a readily available starting material for the synthesis of functionalized six-membered ring systems. The preparation involves hydride abstraction of complex **1** using trityl tetrafluoroborate according to a procedure reported by Fischer (Scheme 1)[2]. Usually, cyclohexadiene is complexed by pentacarbonyliron or nonacarbonyldiiron to the tricarbonyl($\eta^4$-cyclohexadiene)iron (**1**). We have recently reported that quantitative complexation of 1,3-cyclohexadiene is achieved in the presence of 1-aza-1,3-butadienes as tricarbonyliron transfer catalysts[1]. This improved procedure now provides easy access to the tricarbonyliron-complexed cyclohexadienylium cation **2** on a large scale in virtually quantitative overall yield.

Scheme 1




Ar = 4-MeO($C_6H_4$); M = $Fe(CO)_3$

The addition of nucleophiles to tricarbonyliron-complexed dienylium cations is a useful and convenient method for the regio- and stereoselective formation of carbon–carbon bonds and carbon–heteroatom bonds[3]. Regioselectivity derives from the fact, that the nucleophile usually adds to one of the termini of the transition-metal-complexed $\pi$ system (Davies-Green-Mingos rules)[4]. The stereoselectivity generally observed is a result of the sterical demand exhibited by the tricarbonyliron group which directs the nucleophile to the face of the ligand opposite to the transition metal (*anti* selectivity). Therefore, these reactions offer a broad potential for applications to synthetic organic chemistry[5].

Kane-Maguire has demonstrated that nucleophilic attack on the iron-complexed cation **2** is feasible with electron-rich heteroaromatic systems[6] (e.g., pyrrole, indole, imidazole, furan, and thiophene) and with donor-substituted aryl derivatives[7]. We have considered the iron-complexed cation **2** a mild electrophile useful for the electrophilic aromatic substitution of highly donor-substituted arylamines. A procedure involving consecutive iron-induced C–C and C–N bond formation by regioselective electrophilic aromatic substitution of an arylamine and subsequent cyclization should provide a convergent route to functionalized carbazole alkaloids. First we have studied the regio- and stereoselectivity as well as the mechanism of electrophilic substitutions of donor-substituted arylamines with tricarbonyliron-complexed $\eta^5$-cyclohexadienylium cations. These results and a preliminary investigation of the oxidative cyclization to carbazoles are described in this paper in full detail.

The reaction of 2.2 equiv. of *p*-anisidine with the iron-complexed cation **2** in acetonitrile at reflux provides regio- and stereoselectively the complex **3** by a modified literature procedure (Scheme 2)[7d,e]. In this reaction the second equivalent of the arylamine is used as a base in order to trap the hydrotetrafluoroboric acid formed in this process. Even by

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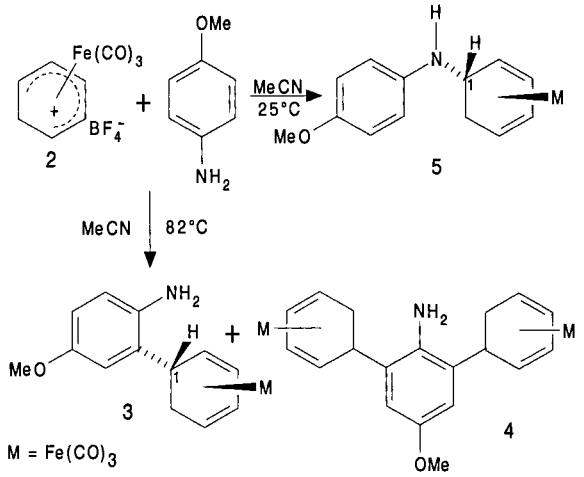
slow addition of the cation **2** to the refluxing solution of *p*-anisidine in acetonitrile the formation of the less polar by-product **4**, resulting from attack of a second equiv. of **2** at the alternative *ortho*-amino position of the arylamine, cannot be avoided (yields; **3**: 55%; **4**: 20%). Both products are readily separated by flash chromatography on silica gel.

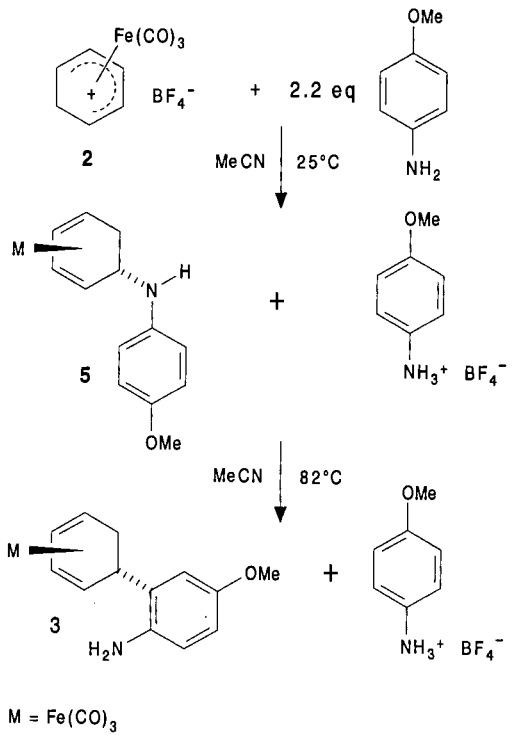
Scheme 2




Treatment of 2.2 equiv. of *p*-anisidine with cation **2** in acetonitrile at room temperature for 30 min leads exclusively to the *N*-alkylated arylamine **5** as the kinetic product of this reaction (Scheme 2)[8]. The rate of *N*-alkylation by the tricarbonyliron-complexed cation is dependent on the basicity of the arylamine[9]. Flash chromatography provides the desired iron complex **5** contaminated with a trace of *p*-anisidine. This observation indicates that the *N*-alkylated arylamine **5** is decomposed to a small extent on silica gel. Nevertheless, the product is of sufficient purity according to its $^1$H-NMR spectrum for further investigations. We wanted to gather more information about the mechanism of this selectivity reversal which is dependent on the reaction temperature. The following reactions have been monitored by thin-layer chromatography (TLC) and/or by isolation and $^1$H-NMR spectroscopy. The iron complexes **3** and **5** show only a slight difference in their $R_f$ values, but they provide a different color on developing the TLC plate with the ceric sulfate/phosphomolybdic acid reagent[10]. In the $^1$H-NMR spectrum both compounds are easily distinguished by the shift of the proton at C-1 whose signal appears as a doublet of triplets at $\delta$ = 3.40 for complex **3** and at $\delta$ = 3.88 for complex **5**.

In a control experiment a mixture of the complex salt **2** and 2.2 equiv. of *p*-anisidine is stirred at room temperature, and the reaction is followed by TLC. Complex **5** is formed rapidly but is unchanged even after 5 h. However, heating of the reaction mixture at reflux temperature for 30 min converts the *N*-alkylated arylamine completely into the product of electrophilic aromatic substitution **3** (Scheme 3). Obviously, at elevated temperature the initially formed kinetic product **5** rearranges to the thermodynamic product **3**. The isolated, pure compound **5** does not rearrange to complex **3** when refluxed in acetonitrile alone or in the presence of *p*-anisidine nor in the presence of acetic acid (as previously reported[7d,e]). We have assumed that the presence of *p*-anisidine hydrotetrafluoroborate which is generated by trapping of hydrotetrafluoroboric acid with the second equiv. of *p*-anisidine is crucial for the transformation of **5** to **3** at higher temperatures. In a further experiment, we have shown that the rearrangement of the isolated pure complex **5** on heating with acid (e.g. acetic acid) is achieved only when additional *p*-anisidine is present as a nucleophile. Thus, when heating a solution of complex **5** in acetonitrile at reflux with acetic acid, rearrangement to complex **3** and traces of dialkylated arylamine **4** occurs after the addition of *p*-anisidine. Obviously, protonation of iron complex **5** at the arylamine nitrogen atom and generation of a leaving group at C-1 of the iron complex initiate the rearrangement to **3** as proposed previously[7d,e]. But the presence of an additional equivalent of *p*-anisidine is necessary to accomplish electrophilic aromatic substitution in the rearrangement process. This observation suggests that the rearrangement of the kinetic product **5** to the thermodynamic product **3** occurs intermolecularly. In order to have a close mimic for the reaction conditions of the electrophilic substitution reaction of *p*-anisidine with cation **2** we have treated the isolated iron complex **5** with the hydrotetrafluoroborate of *p*-anisidine. The *p*-anisidine hydrotetrafluoroborate is prepared by the reaction of the arylamine with an aqueous $HBF_4$ solution (50%) and the salt subsequently dried in high vacuum. A solution of 1 equiv. of the isolated pure complex **5** and 1 equiv. of *p*-anisidine hydrotetrafluoroborate in acetonitrile is stirred for 20 h at room temperature. After this time, TLC analysis indicates already the formation of some

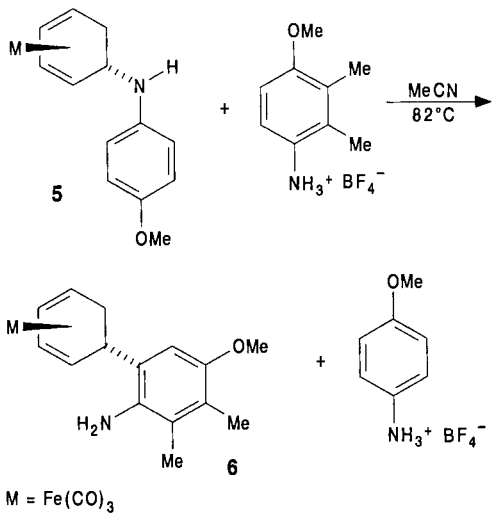
Scheme 3



product **3** together with starting material. For completion of the rearrangement the mixture is heated to reflux for further 45 min. According to TLC analysis some of the dialkylated arylamine **4** is formed again under these reaction conditions. Flash chromatography on silica gel affords the desired iron complex **3** in 44% yield.

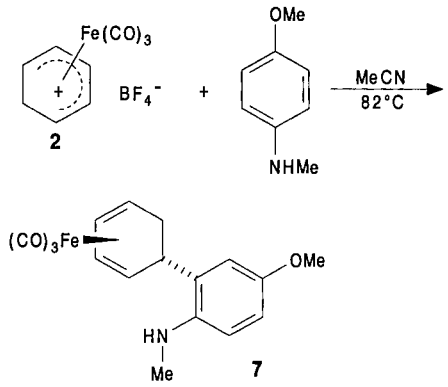
The intermolecular character of this rearrangement has been confirmed by a crossover experiment between the *N*-alkylated arylamine **5** and an equimolar amount of the hydrotetrafluoroborate of 4-methoxy-2,3-dimethylaniline (prepared as described above for the *p*-anisidine hydrotetrafluoroborate). After stirring at room temperature in acetonitrile for 3 h, TLC analysis indicates already the formation of the known[11] iron complex **6** (Scheme 4), which represents a crucial intermediate in our synthesis of 4-deoxycarbazomycin B. Heating the reaction mixture at reflux for 30 min completes the transformation, and subsequent flash chromatography provides iron complex **6** (63% yield). The *C*-alkylated *p*-anisidine is formed only in traces (TLC analysis) and cannot be isolated.

Scheme 4



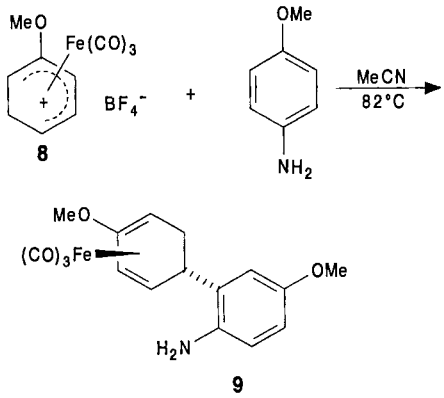

In the following we have tested a series of arylamines for the regioselective electrophilic aromatic substitution using tricarbonyliron-complexed cyclohexadienylium cations with the objective to get access to potential precursors for the synthesis of carbazole derivatives. The reaction of *N*-methyl-*p*-anisidine with the complex salt **2** provides the desired iron complex **7** in 80% yield (Scheme 5). The stereochemistry of **7** has been assigned on the basis of the chemical shift of the proton at C-1 ($\delta$ = 3.36) in comparison with those of the complexes described above. A useful tool for the stereochemical assignment of these complexes is the effect of magnetic anisotropy of the iron atom in $^1$H-NMR spectra. The signal of 1-$H_{syn}$ corresponding to the 1-*anti*-substituted iron complexes is shifted downfield because of the anisotropy of the metal atom (see below). In contrast to *p*-anisidine, the formation of a dialkylated arylamine has not been observed. Obviously, the second electrophilic attack of the iron-complexed cation at the alternative *ortho*-amino position is inhibited due to the steric hindrance caused by the *N*-methyl group.

Scheme 5




The electrophilic substitution reaction of *p*-anisidine with the tricarbonyl($\eta^5$-2-methoxycyclohexadienylium)iron cation **8**[3a,b] affords complex **9** in only 19% yield (Scheme 6). The 2-methoxy-substituted cation is reported to be much less reactive towards nucleophilic attack compared to the parent compound **2**[7c,9,12]. However, much better results with the 2-methoxy-substituted cation **8** have been obtained in the electrophilic substitution of aniline, *p*-toluidine[7d,e], and 4-methoxy-2,3-dimethylaniline[11].

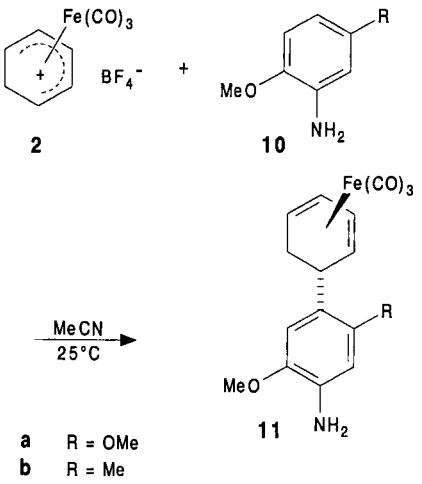
Scheme 6




We have turned our interest to the electrophilic substitution of highly donor-substituted arylamines using the tricarbonyliron-complexed cyclohexadienylium cation **2**. It is known that 3-methoxyaniline, because of its increased nucleophilicity, undergoes C–C bond formation with cation **2** even at room temperature, and it reacts twice to afford exclusively the 4,6-disubstituted 3-methoxyaniline derivative[7d,e]. The second electrophilic substitution by the iron-complexed cation can be avoided by using 2,5-disubstituted anilines **10**. In fact, C–C bond formation with these highly donor-activated arylamines occurs even at room temperature, however, exclusively in the *para* position with respect to the amino group to provide the iron complexes **11** (Scheme 7). This substitution pattern is confirmed by the

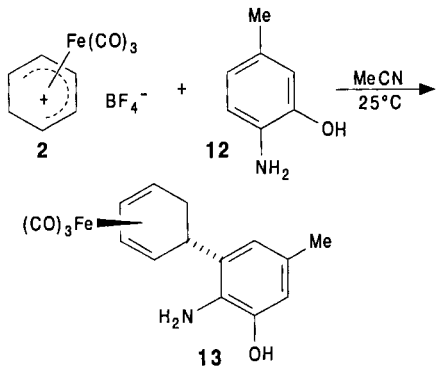
signals of the two aromatic protons of **11a** and **b** which appear as singlets in the $^1$H-NMR spectrum. The stereochemistry of the electrophilic substitution has again been established by the chemical shift of 1-H ($\delta_{1\text{-H}}$: **11a**: 3.70; **11b**: 3.52). Unfortunately, the iron complexes **11** are not suitable for cyclization to carbazole derivatives. The regiochemistry of the products may be explained in steric terms. The only available free *ortho*-amino position is obviously too hindered for the bulky tricarbonyliron-complexed cyclohexadienylium cation **2** by the two adjacent substituents.

Scheme 7



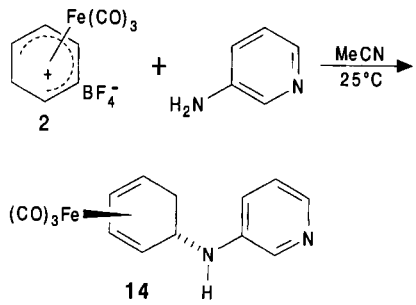

The use of 2,4-disubstituted anilines in the electrophilic substitution reaction with the iron-complexed cation **2** avoids the undesired regioselectivity. Thus, the reaction of **2** with 2-hydroxy-4-methylaniline (**12**), where the *para*-amino position is blocked by a methyl group, takes place at room temperature exclusively in the *ortho* amino position to afford complex **13** (Scheme 8). Again the C–C bond formation (electrophilic aromatic substitution) of the highly donor-substituted arylamine with **2** occurs already at room temperature. With highly activated arylamines cation **2** either reacts directly by electrophilic substitution, or the proton-catalyzed intermolecular rearrangement of the initially formed *N*-alkylated derivative has a considerably higher driving force and takes place at room temperature. In any case, it is interesting for us to learn that electrophilic substitution of aryl derivatives bearing a free hydroxy and a free amino group is easily achieved by using iron-complexed cations.

Scheme 8



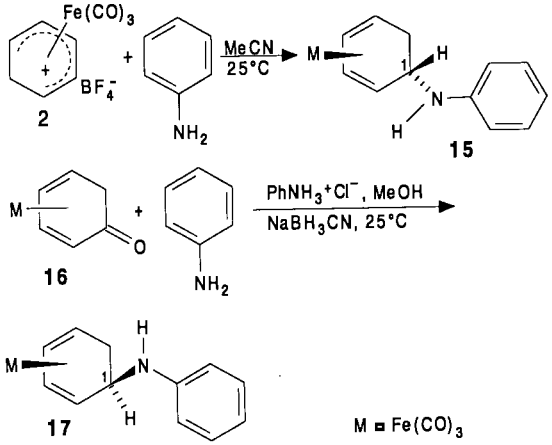

Substituted pyridines have been found to provide the corresponding pyridinium salts in the reaction with tricarbonyliron-complexed cyclohexadienylium cations[13]. The reaction of 3-aminopyridine with the iron-complexed cation **2** in acetonitrile both at room temperature and at reflux temperature affords exclusively the *N*-substituted product **14** (Scheme 9). The *N*-alkylation is supported by the presence of 4 heteroaromatic protons as indicated by the $^1$H-NMR spectrum and the chemical shift of the proton at C-1 ($\delta$ = 3.97). The fact that at reflux temperature no C–C bond formation is observed is in agreement with the report that the reaction of 4-nitroaniline with cation **2** affords exclusively the *N*-substituted product even at higher temperatures[7d,e]. Obviously, owing to the low electron density of the aromatic systems of both amines the latter cannot undergo electrophilic substitution on treatment with tricarbonyliron-complexed cations.

Scheme 9




In order to confirm the *anti* selectivity of the alkylation of arylamines using tricarbonyliron-complexed cations we have decided to synthesize the corresponding *syn* complex for comparison (*syn* and *anti* denote the orientation of the substituent in position 1 relative to the tricarbonyliron group referred to the cyclohexadiene ring plane). The reaction of aniline with cation **2** in acetonitrile at room temperature affords the 1-*anti*-substituted complex **15**[8] (Scheme 10). The tricarbonyliron-complexed cyclohexadienone **16** has been shown to provide the 1-*syn*-hydroxy compound on reduction with sodium borohydride[3a]. Thus, we have anticipated that the reductive amination of **16** with aniline should lead to the tricarbonyliron cyclohexadiene complex with the aniline substituent in the 1-*syn* position, because the reduction of the intermediate iminium cation is expected to take place from the face opposite to the iron atom (*anti* selectivity). This reduction should enforce the anilino group to be located on the same side as the metal atom and therefore give rise to a *syn*-stereospecific process.

Scheme 10

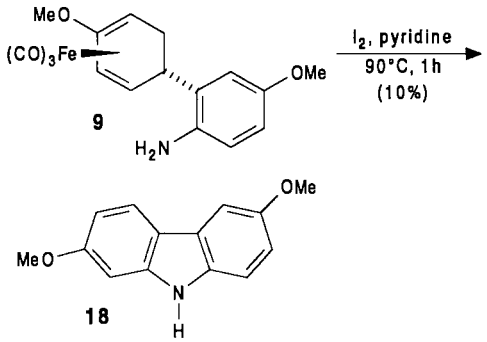



Reductive amination of the cyclohexadienone **16** with aniline in the presence of aniline hydrochloride and sodium cyanoborohydride provides stereoselectively the 1-*syn* complex **17** (Scheme 10). Structural support for the 1-*syn* complex **17** derives from a comparison of its $^1$H-NMR spectrum with that of the 1-*anti* complex **15** utilizing the effect of magnetic anisotropy of the iron atom in $^1$H-NMR spectroscopy[8]. A considerably larger shielding of the *anti* protons relative to the *syn* protons is found in the $^1$H-NMR spectra of ($\eta^4$-cyclohexadiene)transition-metal complexes[14]. The signal of the *syn* proton at C-1 of the *anti* complex **15** (200 MHz, $CDCl_3$: $\delta$ = 3.99) is shifted downfield with respect to the resonance line of the 1-*anti* proton of the *syn* complex **17** (200 MHz, $CDCl_3$: $\delta$ = 3.52). This result demonstrates the feasibility of a direct and stereospecific access to 1-*syn*-arylamino-substituted tricarbonyl(cyclohexadiene)iron complexes and confirms the stereochemical assignments made earlier.

It has been shown by Birch that the oxidative cyclization of tricarbonyl($\eta^4$-cyclohexadiene)iron complexes with an enol (β-diketone or β-oxoester) on a side chain can be used for the synthesis of tricarbonyliron-complexed *cis*-4a,7a-dihydrobenzofurans[15]. The reaction conditions usually employed in these cyclizations are heating under reflux in benzene for 2 h with commercial manganese dioxide or lead dioxide. Pearson has applied this method to the cyclization of a wide range of hydroxyalkyl-substituted tricarbonyl(cyclohexadiene)iron complexes[16]. A $Tl^{3+}$-induced addition of ethanol to tricarbonyl($\eta^4$-cyclohexadiene)iron, as an intermolecular example of this reaction, has been observed by Lewis[17]. The oxidative cyclization by an amino group located in the side chain would lead to nitrogen heterocycles, however, there is only one report of such an oxidation[18]. We are convinced that the exploitation of this reaction would provide a method with high potential for alkaloid synthesis. In a preliminary study of the utility of this method we have investigated the oxidative cyclization of the iron complexes **3**, **7**, **9**, and **13** which represent potential precursors for the synthesis of oxygenated carbazoles. In fact, we have found that the oxidative cyclization of tricarbonyl(cyclohexadiene)iron complexes using the appropriate reaction conditions opens up a direct route to the desired tricyclic carbazole derivatives.

However, the application of the previously described method (reaction with iodine in pyridine at 90 °C for 1 h)[18] to the reaction of iron complex **9** gave 2,6-dimethoxycarbazole (**18**) in only 10% yield (Scheme 11). The oxidative cyclization of tricarbonyl(cyclohexadiene)iron complexes to oxygen heterocycles has been accomplished with manganese dioxide[15,16b]. The attempt to achieve cyclization by oxidation with commercial manganese dioxide[19] has led to decomposition of the starting material even with variation of temperature and solvent. We have explained these disappointing results by the effect of the donor substituents of our precursor which give rise to the formation of an oxidation-sensitive carbazole. Therefore, we have reinvestigated the reported cyclization of iron complex **19**[18] to 3-methylcarbazole (**21**).

Scheme 11

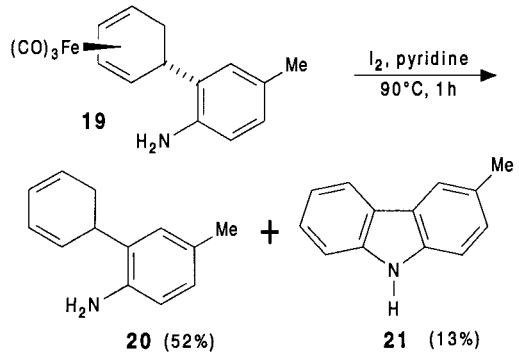



Our attempts to reproduce the described procedure of the cyclization of **19** (treatment with iodine in pyridine for 1 h at 90 °C)[18] have predominantly led to demetalation without cyclization and provided the corresponding free ligand **20** (colorless oil) in 52% yield along with 3-methylcarbazole (**21**) (colorless crystals, 13% yield) only as the minor product (Scheme 12). The carbazole **21** is slightly less polar than the cyclohexadiene derivative **20**. Due to their different $R_f$ values the two products may be separated by flash chromatography on silica gel and subsequently completely characterized (see Experimental). Because of this surprising result (in ref.[18] a yield of 69% is reported for the carbazole **21**) we have repeated the reaction several times and payed close attention to follow the literature procedure exactly with respect to the scale of the reaction and conditions. The results are consistent and reveal that both products are always formed in a ratio of ca. 4:1 in favor of the cyclohexadiene derivative **20**. Therefore, we have investigated alternative reagents for the oxidative cyclization to carbazole derivatives.

Treatment of complex **19** with manganese dioxide at room temperature, commercial manganese dioxide[19] in dichloromethane as well as very active manganese dioxide[20] in toluene, results only in slow decomposition of the starting material. In a further experiment we have tested the efficiency of thallium trifluoroacetate which has already been used as the oxidant in tricarbonyl(cyclohexadiene)iron

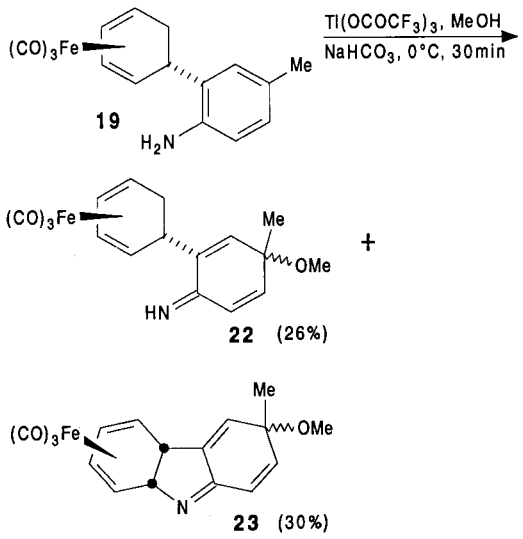
chemistry for the addition of alcohols[16a,17] and for iminoquinone cyclizations[21].

Scheme 12



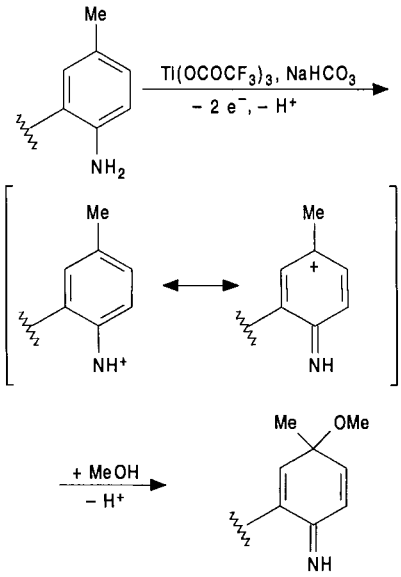

The reaction of complex **19** with thallium trifluoroacetate and sodium hydrogen carbonate as a base in methanol for 30 min at 0°C affords the iron complexes **22** and **23** which can be separated by flash chromatography (Scheme 13). The noncyclized imine complex **22** and the carbazole derivative **23** are both obtained as diastereomeric mixtures in a 1:1 ratio, which is evident by the doubling of the signals of the methyl and methoxy groups in the $^1$H-NMR spectrum. The chemical shifts of the methyl groups ($\delta$ = 1.32/1.35 for **22** and 1.32/1.36 for **23**) are typical of aliphatic methyl groups and therefore indicate that the aromatic system is lost.

Scheme 13




The formation of complex **22** can be explained by the assumption that the primary oxidative attack by the thallium(III) reagent takes place at the arylamine and not at the tricarbonyl(cyclohexadiene)iron moiety. This leads to a nitrenium cation intermediate (Scheme 14) which is attacked by methanol as the nucleophile in the *para* position with respect to the amino group to provide the thermodynamically favored cross-conjugated dienimine.

Scheme 14



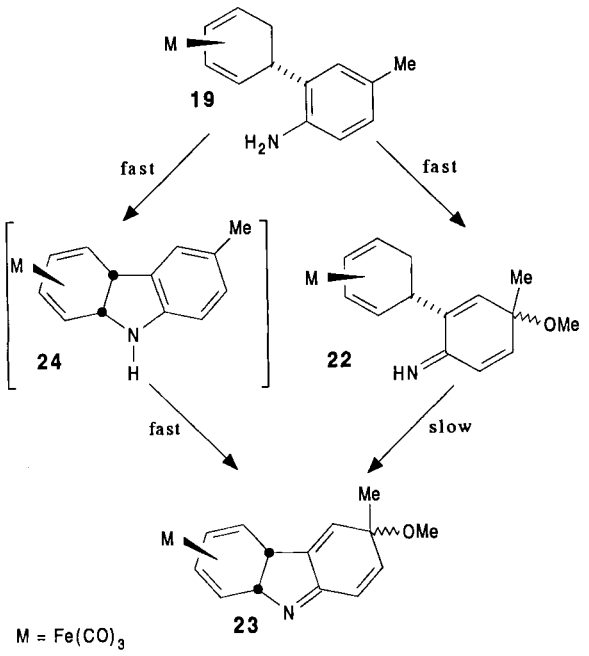

There are two possible pathways for the formation of the carbazole derivative **23** (Scheme 15). First, compound **23** can be formed by the oxidative cyclization of the dienimine **22** which is a byproduct of this reaction. Second, the oxidative cyclization of the iron complex **19** to the 4a,9a-dihydro-9*H*-carbazole **24** takes place first. Chemoselective oxidation of the aromatic ring to the dienimine, as described in Scheme 14, following the cyclization step would also afford complex **23**. In order to solve the question by which reaction sequence the carbazole derivative **23** is formed, we have investigated the cyclization of the iron complex **22**. The oxidations have carefully been monitored by TLC. Treatment of complex **22** with thallium trifluoroacetate under the usual conditions gives almost no turnover after 1 h at 0°C. But workup after 24 h at room temperature affords the cyclization product **23** in 19% yield along with a trace of the starting material. Alternatively, the cyclization of the iron complex **22** is achieved by oxidation with very active manganese dioxide[20] in dichloromethane (Scheme 15). Also with the heterogeneous oxidant 24 h at room temperature are required for the transformation of **22** to the carbazole derivative **23** (27% yield).

The oxidative cyclization of the iron complex **22** to the carbazole derivative **23** is obviously a very slow process. One has to recall that the direct oxidation of iron complex **19** with thallium(III) trifluoroacetate provides the products **22** and **23** in 26% and 30% yield after 30 min at 0°C (Scheme 13). Therefore, the 4a,9a-dihydro-9*H*-carbazole **24** is considered the crucial intermediate in the oxidation to **23**. When we start with the iron complex **19** both reaction pathways described in Scheme 15 are followed parallel on oxidation with thallium(III) trifluoroacetate. However, the slow cyclization of **22** contributes only insignificantly to the formation of **23**.

Attempts to demetalate the carbazole derivative **23** by using trimethylamine *N*-oxide[22] have led only to decomposition of the starting material. The generation of 3-meth-

ylcarbazole (**21**), which may have been formed by elimination of methanol and subsequent tautomerization, has not been observed. Thus, the present cyclization with thallium(III) trifluoroacetate leading to **23** is not considered a promising route to the aromatized carbazole.

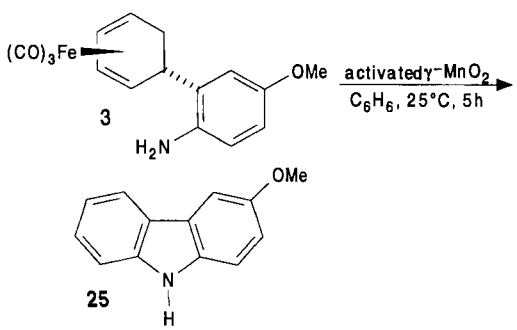
Scheme 15




We have found that the use of especially activated manganese dioxides such as those described by Fatiadi opens up a direct route to oxygenated carbazoles under mild reaction conditions (oxidative cyclization at room temperature).

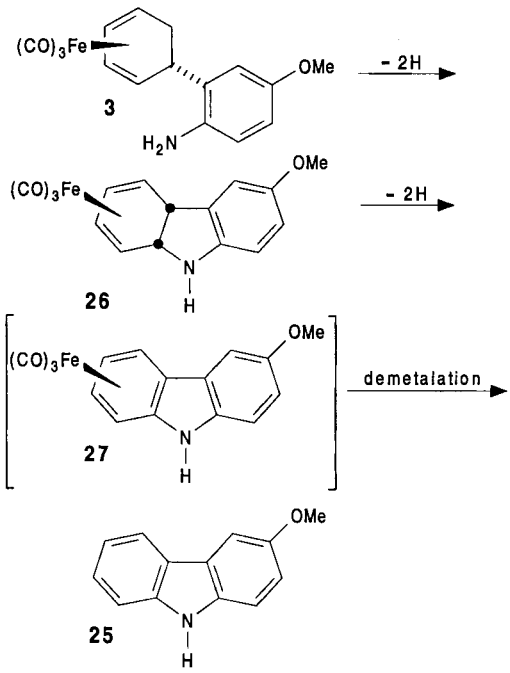
The oxidation of the iron complex **3** with freshly prepared activated γ-manganese dioxide[20] in benzene at room temperature provides directly 3-methoxycarbazole (**25**)[23] in 29% yield (Scheme 16). However, attempts to achieve oxidative cyclization of the iron complexes **7** and **13** have led exclusively to decomposition of the starting material under various reaction conditions [commercial $MnO_2$[19], very active $MnO_2$[20], $Tl(OCOCF_3)_3$]. These results indicate that iron-mediated oxidative cyclizations to *N*-alkylcarbazoles and 1-hydroxycarbazoles are not feasible under the reaction conditions used above.

Scheme 16




For the one-pot transformation of iron complex **3** to 3-methoxycarbazole (**25**) we propose a mechanism involving the steps cyclizing dehydrogenation, aromatizing dehydrogenation, and demetalation (Scheme 17). The cyclization of **3** leads to the tricarbonyliron-complexed *cis*-4a,9a-dihydro-9*H*-carbazole **26**, a potentially stable 18-electron complex. Aromatization of **26** generates the 20-electron ($\eta^6$-arene)tricarbonyliron complex **27** which demetalates spontaneously to 3-methoxycarbazole (**25**). A similar mechanism is assumed for the cyclization of complex **9** to 2,6-dimethoxycarbazole (**18**).

Scheme 17




The described methodology of consecutive iron-induced C–C and C–N bond formation opens up the way to a direct synthesis of many naturally occurring carbazole alkaloids which are oxygenated in the positions 3 or 2 and 6[24]. The efficiency of the sequence cyclization/aromatization/demetalation requires optimization which is presumably achieved by using more specific oxidants. Further applications of this process are under investigation.

This work was supported by the *Deutsche Forschungsgemeinschaft* (grant Kn 240/4-2) and the *Fonds der Chemischen Industrie.* Generous gifts of carbonyliron compounds by Dr. *G. Steiner* (BASF AG, Ludwigshafen) are gratefully acknowledged. We are indebted to Dr. *V. Wray* [Gesellschaft für Biotechnologische Forschung (GBF), Braunschweig-Stöckheim] for $^{13}$C-NMR measurements.

## Experimental

Melting points: Reichert hot stage. – UV: Beckman 3600. – IR: Perkin-Elmer 580 and 1710 (FT-IR). – $^1$H- and $^{13}$C-NMR: Bruker WP-200, AM-300, and WM-400; internal standard: tetramethylsilane or chloroform; coupling constants in Hz. – MS: Finnigan MAT-312; ionization potential of 70 eV. – Elemental analyses: Heraeus CHN-Rapid. – Flash chromatography: Baker silica gel

(0.03–0.06 mm), with eluents given. Generally, all reactions have been carried out by using dry and degassed solvents under an inert gas.

*Tricarbonyl[N-($\eta^4$-cyclohexa-2,4-dienyl)-4-methoxybenzeneamine]iron* (**5**): A solution of complex salt **2** (921 mg, 3.01 mmol) in acetonitrile (25 ml) is added to a solution of *p*-anisidine (814 mg, 6.62 mmol) in acetonitrile (20 ml) at room temperature. The solution is stirred for 30 min under nitrogen. Removal of the solvent in vacuo and flash chromatography of the residue on silica gel [ethyl acetate/light petroleum ether (1:3)] afford the iron complex **5** (672 mg, 65%) as yellow crystals. – For spectroscopic data see ref.[7e].

*Tricarbonyl[2-($\eta^4$-cyclohexa-2,4-dienyl)-4-methoxybenzeneamine]iron* (**3**)

1. *Direct Synthesis:* A solution of the complex salt **2** (3.30 g, 10.8 mmol) in acetonitrile (90 ml) is added over a period of 40 min under nitrogen to a refluxing solution of *p*-anisidine (2.94 g, 23.9 mmol) in acetonitrile (35 ml). After the addition is completed, the reaction mixture is heated at reflux temperature for further 30 min. The solvent is evaporated, and the residue is taken up in a small volume of dichloromethane. Flash chromatography on silica gel [diethyl ether/light petroleum ether (1:2)] provides the dialkylated arylamine **4** as the less polar fraction (625 mg, 20%) and iron complex **3** as the more polar fraction (2.04 g, 55%), yellow crystals. – IR (KBr): $\tilde{\nu}$ = 3432 $cm^{-1}$, 3366, 2049, 1975, 1958, 1494, 1278, 1212, 619, 564. – $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 1.59 (m, 1H), 2.40 (ddd, *J* = 15, 11, 3.8, 1H), 3.14 (m, 1H), 3.19 (m, 1H), 3.32 (br. s, 2H), 3.40 (dt, *J* = 11, 3.6, 1H), 3.75 (s, 3H), 5.52 (m, 2H), 6.58 (m, 2H), 6.72 (m, 1H). – MS (90°C): *m/z* (%) = 341 (11) [$M^+$], 313 (9), 285 (31), 257 (48), 255 (52), 178 (100).

$C_{16}H_{15}FeNO_4$ (341.15) Calcd. C 56.33 H 4.43 N 4.11
Found C 56.13 H 4.42 N 3.90

2. *Rearrangement of Complex* **5** *to Complex* **3**: A solution of *p*-anisidinium hydrotetrafluoroborate (39.0 mg, 0.18 mmol) in acetonitrile (1 ml) is added to a solution of iron complex **5** (63.0 mg, 0.18 mmol) in acetonitrile (5 ml). The mixture is stirred for 20 h at room temperature (TLC control indicates already formation of some product **3**) and subsequently heated at reflux temperature for 45 min to complete the reaction. Removal of the solvent and flash chromatography of the residue on silica gel [ethyl acetate/light petroleum ether (1:3)] afford along with some of the dialkylated arylamine **4** the iron complex **3** (28.0 mg, 44%), yellow crystals.

*Tricarbonyl[6-($\eta^4$-cyclohexa-2,4-dienyl)-4-methoxy-2,3-dimethylbenzeneamine]iron* (**6**): A solution of 4-methoxy-2,3-dimethylanilinium tetrafluoroborate (50.0 mg, 0.21 mmol) in acetonitrile (2 ml) is added to a solution of the iron complex **5** (71.0 mg, 0.21 mmol) in acetonitrile (4 ml). After stirring at room temperature for 3 h, TLC control indicates already formation of some product **6**. For completion of the reaction the mixture is heated at reflux for 30 min. Evaporation of the solvent and flash chromatography of the residue on silica gel [ethyl acetate/light petroleum ether (1:3)] provide the known iron complex **6** (48.0 mg, 63%), light yellow crystals[11].

*Tricarbonyl[2-($\eta^4$-cyclohexa-2,4-dienyl)-4-methoxy-N-methylbenzeneamine]iron* (**7**): A solution of the complex salt **2** (1.50 g, 4.90 mmol) in acetonitrile (30 ml) is added over a period of 30 min under argon to a refluxing solution of *N*-methyl-*p*-anisidine (1.48 g, 10.8 mmol) in acetonitrile (15 ml). After the addition is completed, the reaction mixture is heated for further 40 min at reflux, and the solvent is removed in vacuo. Flash chromatography [diethyl ether/light petroleum ether (1:3)] of the residue on silica gel provides the iron complex **7** (1.39 g, 80%), yellow crystals; m.p. 85°C. – IR (KBr): = 3441 $cm^{-1}$, 2937, 2050, 1970, 1957, 1510, 1441, 1342, 1280, 1213, 1171, 1067, 1039, 878, 800, 615, 559. – $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 1.54 (m, 1H), 2.38 (ddd, *J* = 15.04, 11.1, 3.86, 1H), 2.82 (s, 3H), 3.15 (m, 2H), 3.36 (dt, *J* = 11.1, 3.65, 1H), 3.76 (s, 3H), 5.52 (m, 2H), 6.53 (d, *J* = 8.68, 1H), 6.69 (dd, *J* = 8.68, 2.89, 1H), 6.79 (d, *J* = 2.89, 1H). – $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 31.67 (q), 31.75 (t), 38.18 (d), 55.74 (q), 60.20 (d), 64.55 (d), 84.97 (d), 85.85 (d), 111.07 (d), 111.29 (d), 113.78 (d), 132.74 (s), 140.69 (s), 151.95 (s), 211.92 (s). – MS (130°C): *m/z* (%) = 355 (2) [$M^+$], 327 (17), 299 (5), 298 (23), 271 (34), 270 (10), 269 (56), 254 (33), 239 (17), 215 (7), 214 (11), 199 (12), 198 (12), 194 (11), 193 (100), 184 (13), 167 (7), 154 (7), 137 (77), 122 (23), 112 (12).

$C_{17}H_{17}FeNO_4$ Calcd. 355.0507 Found 355.0506 (MS)

*Tricarbonyl[2-($\eta^4$-4-methoxycyclohexa-2,4-dienyl)-4-methoxybenzeneamine]iron* (**9**): A solution of the 2-methoxy-substituted complex salt **8** (2.45 g, 7.31 mmol) in acetonitrile (55 ml) is added over a period of 30 min under nitrogen to a refluxing solution of *p*-anisidine (1.98 g, 16.1 mmol) in acetonitrile (25 ml). After the addition is completed the reaction mixture is heated at reflux temperature for further 30 min and the solvent removed in vacuo. Flash chromatography [diethyl ether/light petroleum ether (1:2)] of the residue on silica gel provides iron complex **9** (504 mg, 19%), yellow crystals. – IR ($CHCl_3$): $\tilde{\nu}$ = 2940 $cm^{-1}$, 2860, 2045, 1970 (br.), 1608, 1500, 1485, 1425, 1280, 1025, 910, 625, 612, 578. – $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 1.68 (ddd, *J* = 14.7, 3.6, 2.3, 1H), 2.41 (ddd, *J* = 14.7, 11, 3.6, 1H), 2.74 (dd, *J* = 6.5, 3.4, 1H), 3.21 (dt, *J* = 11, 3.6, 1H), 3.32 (br. s, 2H), 3.42 (dt, *J* = 3.8, 2.3, 1H), 3.68 (s, 3H), 3.75 (s, 3H), 5.27 (dd, *J* = 6.5, 2.3, 1H), 6.58 (m, 2H), 6.72 (m, 1H). – MS (60°C): *m/z* (%) = 371 (1) [$M^+$], 343 (4), 315 (25), 287 (36), 285 (36), 229 (11), 214 (22), 199 (10), 184 (15), 179 (100).

*Tricarbonyl[4-($\eta^4$-cyclohexa-2,4-dienyl)-2,5-dimethoxybenzeneamine]iron* (**11a**): A solution of the complex salt **2** (1.00 g, 3.27 mmol) in acetonitrile (15 ml) is added over a period of 1 h at room temperature under nitrogen to a solution of 2,5-dimethoxyaniline (**10a**) (1.10 g, 7.19 mmol) in acetonitrile (10 ml). The mixture is stirred for further 4 h at room temperature, and the solvent is evaporated. Flash chromatography [diethyl ether/light petroleum ether (1:1)] of the residue on silica gel affords iron complex **11a** (0.72 g, 60%), yellow crystals; m.p. 117°C. – IR (KBr): $\tilde{\nu}$ = 3485 $cm^{-1}$ (br.), 3382 (br.), 2937, 2048, 1969, 1943, 1622, 1598, 1515, 1450, 1331, 1251, 1207, 1043. – $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 1.52 (m, 1H), 2.32 (ddd, *J* = 15.1, 11, 3.8, 1H), 3.15 (m, 2H), 3.70 (dt, *J* = 11, 3.7, 1H), 3.71 (s, 3H), 3.81 (s, 3H), 5.45 (m, 2H), 6.25 (s, 1H), 6.59 (s, 1H). – $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 32.39 (t), 36.33 (d), 56.12 (q), 56.47 (q), 60.88 (d), 66.76 (d), 84.59 (d), 85.61 (d), 99.84 (d), 110.73 (d), 123.95 (s), 135.10 (s), 141.27 (s), 151.41 (s), 212.26 (s). – MS (80°C): *m/z* (%) = 371 (6) [$M^+$], 343 (1), 315 (22), 285 (27), 270 (15), 255 (13), 209 (10), 193 (34), 153 (46), 138 (100), 110 (31).

$C_{17}H_{17}FeNO_5$ (371.2) Calcd. C 55.01 H 4.62 N 3.79
Found C 55.25 H 4.64 N 4.21

*Tricarbonyl[4-($\eta^4$-cyclohexa-2,4-dienyl)-2-methoxy-5-methylbenzeneamine]iron* (**11b**): A solution of complex salt **2** (1.00 g, 3.27 mmol) in acetonitrile (20 ml) is added over a period of 1 h at room temperature under nitrogen to a solution of 2-methoxy-5-methylaniline (**10b**) (0.99 g, 7.19 mmol) in acetonitrile (12 ml). The mixture is stirred for further 3.5 h at room temperature, and the solvent is evaporated. Flash chromatography [diethyl ether/light petroleum ether (1:2)] of the residue on silica gel yields iron complex **11b** (0.57 g, 49%), yellow crystals; m.p. 81°C. – IR (KBr): $\tilde{\nu}$ = 3469 $cm^{-1}$ (br.), 3372 (br.), 2939, 2044, 1994, 1974, 1940, 1623, 1519, 1463, 1323, 1261, 1244, 1218, 1096. – $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 1.50 (m, 1H), 2.14 (s, 3H), 2.35 (ddd, *J* = 15.1, 11.1, 3.9, 1H), 3.16

(m, 2H), 3.44 (br. s, 2H), 3.52 (dt, $J$ = 11.1, 3.7, 1H), 3.84 (s, 3H), 5.49 (m, 2H), 6.45 (s, 1H), 6.60 (s, 1H). – $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 18.62 (q), 32.61 (t), 39.77 (d), 55.80 (q), 60.56 (d), 66.72 (d), 84.69 (d), 85.64 (d), 108.67 (d), 117.04 (d), 127.70 (s), 134.05 (s), 134.29 (s), 145.81 (s), 212.15 (s). – MS (60°C): $m/z$ (%) = 355 (36) [$M^+$], 327 (35), 299 (62), 269 (100), 253 (98), 213 (16), 198 (22), 193 (22), 176 (58), 153 (13).

$C_{17}H_{17}FeNO_4$ (355.2) Calcd. C 57.49 H 4.82 N 3.94
Found C 57.48 H 4.83 N 4.30

*Tricarbonyl[2-(η⁴-cyclohexa-2,4-dienyl)-6-hydroxy-4-methylbenzeneamine]iron* (**13**): A solution of complex salt **2** (1.00 g, 3.27 mmol) in acetonitrile (15 ml) is added over a period of 30 min at room temperature under nitrogen to a solution of 2-hydroxy-4-methylaniline (**12**) (0.89 g, 7.19 mmol) in acetonitrile (15 ml). The mixture is stirred for further 4.5 h at room temperature and finally heated at reflux temperature for 20 min. Removal of the solvent and flash chromatography of the residue on silica gel [diethyl ether/light petroleum ether (1:1)] afford the iron complex **13** (0.51 g, 46%), yellow-brown crystals; m.p. >155°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3402 $cm^{-1}$ (br.), 2925, 2044, 1967, 1588, 1507, 1462, 1300, 1150. – $^1$H NMR (200 MHz, $CDCl_3$): δ = 1.59 (m, 1H), 2.20 (s, 3H), 2.37 (ddd, $J$ = 14.9, 11.1, 3.7, 1H), 3.15 (m, 2H), 3.44 (m, 1H), 5.51 (m, 2H), 6.41 (br. s, 1H), 6.52 (s, 1H). – $^{13}$C NMR and APT (75 MHz, $CDCl_3$): δ = 20.93 ($CH_3$), 31.42 ($CH_2$), 39.02 (CH), 60.27 (CH), 64.95 (CH), 85.03 (CH), 85.71 (CH), 113.70 (CH), 119.29 (CH), 128.56 (C), 129.38 (C), 133.90 (C), 145.16 (C), 211.93 (CO). – MS (90°C): $m/z$ (%) = 341 (2) [$M^+$], 340 (8), 312 (30), 284 (36), 256 (69), 254 (65), 237 (16), 219 (12), 178 (100), 176 (89), 160 (37), 133 (21).

$C_{16}H_{15}FeNO_4$ (341.15) Calcd. C 56.33 H 4.43 N 4.11
Found C 56.40 H 4.52 N 4.29

*Tricarbonyl[N-(η⁴-cyclohexa-2,4-dienyl)-3-aminopyridine]iron* (**14**): 3-Aminopyridine (324 mg, 3.45 mmol) is added to a solution of the complex salt **2** (480 mg, 1.57 mmol) in acetonitrile (15 ml), and the mixture is stirred for 2 h at room temperature under nitrogen. The solvent is subsequently removed in vacuo, the residue is taken up in water and extracted several times with diethyl ether. The combined organic layers are dried with magnesium sulfate. Evaporation of the solvent and flash chromatography [ethyl acetate/light petroleum ether (3.5:1)] of the residue on silica gel provide the iron complex **14** (290 mg, 59%), light yellow crystals. – IR (KBr): $\tilde{\nu}$ = 2050 $cm^{-1}$, 1973, 1955, 1580, 1500, 1480, 1412, 797, 710, 617, 565. – $^1$H NMR (200 MHz, $CDCl_3$): δ = 1.44 (m, 1H), 2.44 (ddd, $J$ = 15, 9.8, 3.9, 1H), 3.03 (m, 1H), 3.18 (ddd, $J$ = 6.2, 3.6, 1.35, 1H), 3.61 (br. d, $J$ = 7.4, 1H), 3.97 (m, 1H), 5.39 (m, 1H), 5.58 (m, 1H), 6.77 (ddd, $J$ = 8.3, 2.9, 1.3, 1H), 7.06 (ddd, $J$ = 8.3, 4.7, 0.6, 1H), 7.93 (m, 2H). – $^1$H-NMR NOE experiments (300 MHz, $CDCl_3$): Irradiation at δ = 2.44; observed NOEs at δ = 1.44, 3.03, 3.97. – $^{13}$C NMR and DEPT (100 MHz, $CDCl_3$): δ = 32.4 ($CH_2$), 51.4 (CH), 56.9 (CH), 61.2 (CH), 83.9 (CH), 87.3 (CH), 118.8 (CH), 123.7 (CH), 136.4 (CH), 138.8 (CH), 143.4 (C), 211.0 (CO). – MS (80°C): $m/z$ (%) = 312 (1) [$M^+$], 311 (3), 284 (35), 256 (37), 254 (34), 236 (100), 234 (25), 150 (64), 56 (61).

$C_{14}H_{12}FeN_2O_3$ (312.1) Calcd. C 53.88 H 3.88 N 8.98
Found C 53.80 H 3.90 N 8.82

*2,6-Dimethoxycarbazole* (**18**): The iron complex **9** (114 mg, 0.31 mmol) is dissolved in dry pyridine (1.5 ml), then iodine (273 mg, 1.07 mmol) is added to the solution, and the mixture is stirred for 1 h at 90°C under nitrogen. After cooling, $Na_2S_2O_4$ (50.0 mg, 0.29 mmol) is added, the mixture is briefly stirred, poured into 10% citric acid (25 ml) and extracted four times with diethyl ether (10 ml). The combined organic layers are dried with magnesium sulfate, and the solvent is evaporated. Flash chromatography of the residue on silica gel [diethyl ether/light petroleum ether (1:1)] affords 2,6-dimethoxycarbazole (**18**) (7.0 mg, 10%). – IR ($CHCl_3$): $\tilde{\nu}$ = 3480 $cm^{-1}$, 2860, 2840, 1630, 1585, 1490, 1465, 1438, 1285, 1160, 1030. – $^1$H NMR (200 MHz, $CDCl_3$): δ = 3.89 (s, 3H), 3.91 (s, 3H), 6.80 (d, $J$ = 2.2, 1H), 6.86 (m, 1H), 6.97 (dd, $J$ = 8.7, 2.5, 1H), 7.27 (dd, $J$ = 8.7, 0.4, 1H), 7.46 (d, $J$ = 2.5, 1H), 7.82 (br. s, 1H), 7.88 (d, $J$ = 8.4, 1H). – MS (110°C): $m/z$ (%) = 227 (100) [$M^+$], 212 (94), 184 (61), 169 (37), 141 (25), 140 (16).

$C_{14}H_{13}NO_2$ Calcd. 227.0946 Found 227.0953 (MS)

*2-(Cyclohexa-2,4-dienyl)-4-methylbenzeneamine* (**20**) *and 3-Methylcarbazole* (**21**): Iodine (350 mg, 2.76 mmol) is added to a solution of the iron complex **19**[18] (255 mg, 0.78 mmol) in dry pyridine (5 ml), and the mixture is stirred for 1 h at 90°C. The solution is cooled, sodium dithionite (100 mg) is added, the resulting mixture is poured into 10% citric acid (50 ml) and extracted several times with diethyl ether. The combined organic layers are washed with brine and dried with magnesium sulfate. Evaporation of the solvent and flash chromatography [ethyl acetate/light petroleum ether (1:9)] of the residue on silica gel provide 3-methylcarbazole (**21**) as the less polar fraction and the free ligand **20** as the more polar fraction.

**20**: Yield 75.0 mg (52%), colorless oil. – IR ($CHCl_3$): $\tilde{\nu}$ = 3460 $cm^{-1}$, 3380, 3035, 2925, 2865, 1621, 1504, 1280. – $^1$H NMR (200 MHz, $CDCl_3$): δ = 6.95 (d, $J$ = 1.6, 1H), 6.87 (br. d, $J$ = 7.9, 1H), 6.60 (d, $J$ = 7.9, 1H), 5.75–6.15 (m, 4H), 3.65 (m, 3H), 2.43 (m, 2H), 2.23 (s, 3H). – $^{13}$C NMR and DEPT (75 MHz, $CDCl_3$): δ = 141.3 (C), 129.5 (CH), 129.3 (CH), 129.1 (C), 127.8 (CH), 126.5 (CH), 125.1 (CH), 123.7 (CH), 116.4 (CH), 36.3 (CH), 23.9 ($CH_2$), 20.5 ($CH_3$). – MS (20°C): $m/z$ (%) = 185 (56) [$M^+$], 184 (100), 169 (24), 152 (10), 120 (10), 107 (47), 106 (21).

$C_{13}H_{15}N$ Calcd. 185.1204 Found 185.1204 (MS)

**21**: Yield 19.0 mg (13%), colorless crystals; m.p. 205°C (ref.[25] 207°C). – IR (KBr): $\tilde{\nu}$ = 3406 $cm^{-1}$, 2921, 1606, 1494, 1461, 1335, 1294, 1244, 807, 748, 729, 592, 573. – $^1$H NMR (200 MHz, $[CD_3]_2CO$): δ = 10.18 (br. s, 1H), 8.06 (d, $J$ = 7.8, 1H), 7.90 (s, 1H), 7.10–7.50 (m, 5H), 2.48 (s, 3H). – MS (20°C): $m/z$ (%) = 181 (100) [$M^+$], 167 (16), 152 (24), 90 (14), 77 (17).

$C_{13}H_{11}N$ Calcd. 181.0891 Found 181.0891 (MS)

*Tricarbonyl[1-(η⁴-cyclohexa-2,4-dienyl)-6-imino-3-methoxy-3-methylcyclohexa-1,4-diene]iron* (**22**) *and Tricarbonyl[η⁴-4b,8a-dihydro-3-methoxy-3-methyl-3H-carbazole]iron* (**23**): The iron complex **19** (74.0 mg, 0.23 mmol) is dissolved in dry methanol (5 ml) at 0°C, then $NaHCO_3$ (63.0 mg, 0.75 mmol) and thallium trifluoroacetate (260 mg, 0.48 mmol) are added to the solution, and the mixture is stirred for 30 min at 0°C. A saturated solution of sodium carbonate is added, the mixture is stirred for 5 min at room temperature and subsequently filtered through a short pad of Celite. The Celite is carefully washed with ethyl acetate. A saturated solution of sodium hydrogen carbonate is added to the combined filtrates, the organic layer is separated, and the aqueous layer is extracted with ethyl acetate. The combined organic layers are dried with magnesium sulfate, and the solvent is removed in vacuo. Flash chromatography [ethyl acetate/light petroleum ether (1:3)] of the residue on silica gel affords the iron complex **22** as the less polar fraction and the iron-complexed carbazole derivative **23** as the more polar fraction.

**22**: Yield 21.0 mg (26%), red crystals (1:1 diastereomeric mixture). – IR (KBr): $\tilde{\nu}$ = 2049 $cm^{-1}$, 1991, 1959, 1572, 1086, 883, 616, 516. – $^1$H NMR (200 MHz, $CDCl_3$): δ = 6.05–6.30 (m, 3H), 5.48 (m, 2H), 3.57 (m, 1H), 3.00–3.20 (m, 2H), 3.10/3.03 (s, 3H), 2.36 (m, 1H), 1.26–1.41 (m, 1H), 1.35/1.32 (s, 3H). – MS (100°C): $m/z$ (%) = 327 (3) [$M^+$ – CO], 326 (7), 298 (15), 295 (17), 271

(60), 269 (51), 254 (16), 239 (100), 238 (87), 237 (18), 182 (31), 163 (52).

$C_{16}H_{17}NO_3Fe$ [$M^+ - CO$] Calcd. 327.0558
Found 327.0558 (MS)

**23**: Yield 24.0 mg (30%), light brown crystals (1:1 diastereomeric mixture). – IR (KBr): $\tilde{\nu}$ = 2929 $cm^{-1}$, 2054, 1964, 1080, 611, 564. – $^1H$ NMR (200 MHz, $CDCl_3$): δ = 6.52 (d, *J* = 10.0, 1H), 6.19 (br. d, *J* = 10.0, 1H), 5.76 (br. s, 1H), 5.37 (m, 2H), 4.75 (m, 1H), 3.46 (m, 1H), 3.15–3.40 (m, 2H), 3.11/3.02 (s, 3H), 1.36/1.32 (s, 3H). – MS (80°C): *m/z* (%) = 353 (2) [$M^+$], 325 (20), 297 (19), 269 (14), 254 (15), 237 (47), 181 (100), 167 (15), 161 (21).

$C_{17}H_{15}NO_4Fe$ Calcd. 353.0350 Found 353.0351 (MS)

*Tricarbonyl[$\eta^4$-4b,8a-dihydro-3-methoxy-3-methyl-3H-carbazole]iron* (**23**)

1. *Cyclization of Complex* **22** *with Thallium Trifluoroacetate:* The iron complex **22** (26.0 mg, 0.07 mmol) is dissolved in dry methanol (3 ml) at 0°C, then $NaHCO_3$ (9.0 mg, 0.11 mmol) and thallium trifluoroacetate (45.0 mg, 0.08 mmol) are added to the solution, and the mixture is stirred for 24 h at room temperature. A saturated solution of sodium carbonate is added, the mixture is stirred for 5 min at room temperature and then filtered through a short pad of Celite which is subsequently washed with ethyl acetate. A saturated solution of sodium hydrogen carbonate is added to the combined filtrates, the organic layer is separated, and the aqueous layer is extracted with ethyl acetate. The combined organic layers are dried with magnesium sulfate. Evaporation of the solvent and flash chromatography [ethyl acetate/light petroleum ether (1:3)] of the residue on silica gel provide complex **23** (5.0 mg, 19%), light brown crystals (1:1 diastereomeric mixture).

2. *Cyclization of Complex* **22** *with Very Active Manganese Dioxide:* The iron complex **22** (26.0 mg, 0.07 mmol) is dissolved in dry dichloromethane (4 ml), then very active manganese dioxide[20] (130 mg) is added to the solution, and the mixture is stirred for 24 at room temperature. Removal of the oxidant by filtration through a short pad of Celite, evaporation of the solvent and flash chromatography [ethyl acetate/light petroleum ether (1:3)] of the residue on silica gel afford complex **23** (7.0 mg, 27%), light brown crystals (1:1 diastereomeric mixture).

*3-Methoxycarbazole* (**25**): A solution of the iron complex **3** (300 mg, 0.88 mmol) in dry benzene (5 ml) is added to a suspension of freshly prepared active γ-manganese dioxide[20] (1.5 g) in dry benzene (25 ml), and the mixture is stirred for 5 h at room temperature under nitrogen. Filtration through a short pad of Celite, removal of the solvent in vacuo and flash chromatography [diethyl ether/light petroleum ether (1:3)] of the residue on silica gel provide 3-methoxycarbazole (**25**) (50.0 mg, 29%), colorless crystals. – UV (EtOH): $\lambda_{max}$ = 351 nm, 338, 299, 295 (sh), 261, 250, 228 (qual.). – IR (KBr): $\tilde{\nu}$ = 3405 $cm^{-1}$, 2843, 1497, 1484, 1462, 1439, 1333, 1296, 1285, 1256, 1224, 1211, 1174, 1034, 844, 821, 749, 728. – $^1H$ NMR (300 MHz, $CDCl_3$): δ = 3.90 (s, 3H), 7.04 (dd, *J* = 8.8, 2.5, 1H), 7.16–7.40 (m, 4H), 7.54 (d, *J* = 2.5, 1H), 7.82 (br. s, 1H), 8.01 (d, *J* = 7.8, 1H). – MS (90°C): *m/z* (%) = 197 (99) [$M^+$], 182 (100), 154 (37).

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