Organometallic Complexes in Synthesis. Part 16.[1] Reactions of Tricarbonyl(cyclohexadienyl)iron(1+) Salts with Aromatic Amines

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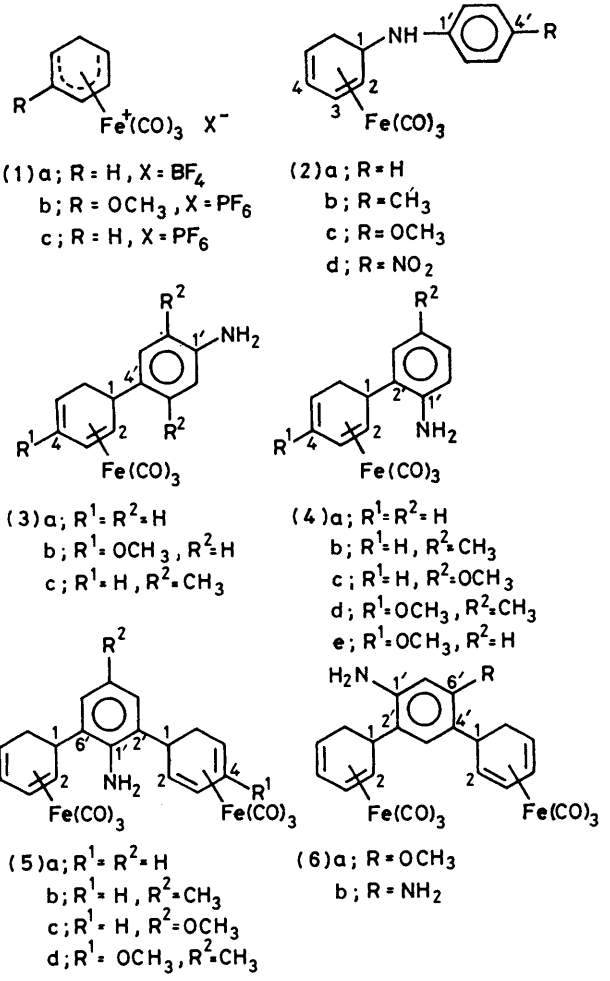
Tricarbonyl(cyclohexadienyl)iron(1+) salts of the type (1) cause *C*- or *N*-alkylation of aromatic amines depending on the conditions used. The best procedure involves formation of the salt *in situ* from an alkoxy-complex in the presence of a small proportion of acid. Attempts to extend the reaction to alkylate 6-amino-5,8-dimethylisoquinoline, to obtain an intermediate for the synthesis of ellipticine, resulted, instead, in irreversible alkylation at the pyridine nitrogen.

NUCLEOPHILIC additions to tricarbonyl(cyclohexadienyl)iron(1+) salts provide a convenient means of C–C bond formation; the resulting complexes can be converted into organic products with specific substitution patterns.[2] Alkylation of aromatic compounds has been observed in cases where the aromatic ring is activated by substituents. Thus whereas benzene and anisole are inert, 1,3- and 1,3,5-methoxy-substituted benzenes give alkylation products.[3] Reactions with aniline,[4] pyrroles,[5] indoles,[6] furan and thiophen,[5] ferrocene,[7] and aryl-$SiMe_3$ or aryl-$SnMe_3$ compounds [8] have been reported.

We recently described [2] the *C*-substitution of *p*-toluidine by the tricarbonyl(cyclohexadienyl)iron(1+) cation (1a), and the conversion of the product into 3-methylcarbazole. The process is noteworthy for several reasons. The carbazole skeleton is formed by a junction of two six-membered rings in which the C–C bond is formed first. Activation for this step is provided by the NH_2 group, which is subsequently employed to form the carbazole product. The electrophilic species does not require organic substituents to promote its reactivity, since the transition-metal complex is itself a stabilised cationic species used as a PF_6^- or BF_4^- salt. Formation of the C–N bond to complete the carbazole skeleton proceeds under mild conditions with detachment of the metal and aromatisation. This paper indicates further the scope of the reaction of tricarbonyl(cyclohexadienyl)iron(1+) salts with aromatic amines, and describes attempts to extend the process for the synthesis of the pyrido[4,3-*b*]carbazole antitumour agent, ellipticine. Part of this work has been the subject of a preliminary communication.[9]



RESULTS AND DISCUSSION

Reactions with Aromatic Amines.—When mixed at room temperature with the salt (1a), aniline, *p*-toluidine, and *p*-anisidine give solely the *N*-alkylation products (2a—c). The rate of *N*-alkylation has been shown [10] to depend markedly on amine basicity. However, if the reaction mixture is heated, electrophilic attack on the aromatic ring occurs and *C*-alkylation products are obtained. As expected, aniline reacts at either the *ortho*- or the *para*-position to give a mixture of products (3a) and (4a). When the *para*-position is blocked, *ortho*-substitution occurs in high yield to give (4b or c). A small quantity of the disubstituted product (5b or c) was also isolated. Initially the *N*-alkylation product (2c) predominated in the product from addition of *p*-anisidine to (1a), but this was converted into the *C*-alkylation product (4c) as the reaction progressed. Irreversible production of (4c) presumably follows an acid-catalysed re-formation of (1a). In accord with this

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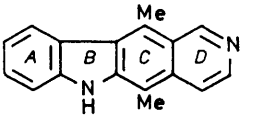
view, (2c) is unchanged if heated alone or with *p*-anisidine, but rearranges after addition of acetic acid.

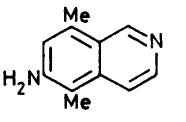
Complete *C*-alkylation required 2 equiv. of the amine, 1 equiv. being protonated by the acid produced during the reaction. *N*-Alkylation of aniline at room temperature was examined by monitoring the intensities of the characteristic M–CO stretching frequencies of (1a) and (2a). In this case *ca.* 10 equiv. of the amine were required before the salt was completely consumed. This further supports the assertion that, whereas the *C*-alkylation is irreversible, *N*-alkylation is reversible under the conditions used. Equilibrium constants for *N*-alkylation of *p*-toluidine by (1a), (1b), and $[(\eta^5\text{-}C_7H_9)Fe(CO)_3][BF_4]$ have subsequently been reported.[11] When the aromatic ring was further activated by a 3-methoxy- or 3-amino-substituent, only 1.5 equiv. were required for complete reaction. Even at room temperature only the disubstituted products (6a and b) were isolated. Deactivation of the aromatic ring can prevent *C*-alkylation: the salt (1a) and 4-nitroaniline gave only the *N*-alkylation product (2d) under a variety of conditions. It has been shown [12] that the salt (1b) is considerably less reactive than the unsubstituted salt (1a). The alkylation of aniline and *p*-toluidine with (1b) was examined to determine whether nuclear substitution was also inhibited by deactivation of the electrophile. The normal *C*-alkylation products (3b), (4e), (4d), and (5d) were obtained, however, demonstrating that the reaction is compatible with a variety of substituents on (1). The nature of substitution on the aromatic ring, on the other hand, is crucial to the course of the reaction.

Studies Related to the Synthesis of Ellipticine.—Since the disclosure [13] of potentially useful tumour inhibition by ellipticine (7) and its analogues, much attention has been given to the synthesis of the pyridocarbazole ring system.[14] Our recent formation [2,9] of carbazoles by alkylation of (1a) and subsequent cyclisation and aromatisation led us to examine the synthesis of pyrido-[3,4-*b*]carbazoles, and in particular ellipticine, by an extension of this procedure. Such a process would introduce ring *A* by alkylation of the known [15] isoquinoline (8), which bears the correct substitution pattern to form rings *C* and *D* of ellipticine. The availability [2] of specifically substituted tricarbonyl(cyclohexadienyl)-iron(1+) salts to allow access to products with substituents on ring *A* is an advantage to this approach. The strategic importance of a convergent approach based on the final formation of ring *B* has been stressed recently by other authors.[16] We reasoned that, provided fusion to the pyridine ring did not excessively deactivate the aromatic amine, equilibration of *N*-alkylation products should ultimately lead to irreversible *C*-alkylation of (8) at the only unsubstituted position on the more electron-rich ring.

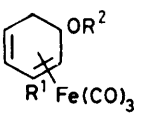
Such an approach would be more attractive if the addition reaction could be modified to avoid the need for a two-fold excess of the amine. Since the second equiv. is required to neutralise acid formed in the reaction, the problem could be avoided by employing a catalytic quantity of acid to generate the salt *in situ* from a neutral complex. Tricarbonyl(η^4-5-alkoxy-1,3-cyclohexadiene)iron(0) complexes of type (9) equilibrate [17] by reversible formation of the η^5-salt in dilute acid. Reaction of *p*-toluidine with the complex (9a) gave the *C*-alkylation product in good yield by displacement of ethanol.



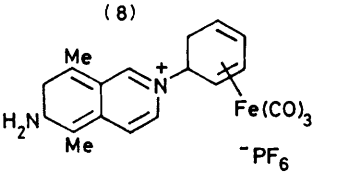
(7)



(8)



(9)a; R^1=CH_3, R^2=C_2H_5



(10)

Regrettably, all attempts to alkylate (8) by reaction with (1c) at reflux in acetonitrile gave no isolable products. At lower temperature a rapid reaction resulted in *N*-alkylation of the pyridine ring. This reaction is apparently irreversible and attempted equilibration of the product (10) to achieve *C*-alkylation was unsuccessful. Analogous formation of pyridinium salts by alkylation of (1a) has been reported,[10,18,19] and electrophilic addition to the 2-position of (8) is known.[20] Support for the proposed structure (10) is drawn from the high frequency of the i.r. carbonyl stretching. The n.m.r. spectrum shows a downfield shift of the 1β-H signal to δ 5.20, consistent with a proton at a position substituted by the isoquinolinium nitrogen. N.m.r. assignments for (10) were determined by spin-decoupling experiments. Irradiation at δ 5.20 caused signals at δ 3.12, 2.86, and 1.78 to collapse, whereas irradiation at δ 5.86 affected only resonances at 3.12 and 3.28. The NH_2 resonance at δ 5.74 was identified by exchange with D_2O. Irradiation at δ 8.87 simplified the 2 H multiplet at δ 7.89 to an AB system of two resonances at very similar chemical shifts. Conversely, irradiation at δ 7.89 caused the narrow (*J* 1 Hz) doublet at 8.87 to collapse to a sharp singlet, but left the resonance at δ 7.14 unchanged. This latter signal, then, must correspond to the isolated proton at C-7′. The methyl groups were distinguished by irradiation at this frequency. This removed the allylic coupling between 7′-H and 8′-CH_3, causing the broad singlet at δ 2.62 to sharpen.

The desired alkylation of (8) at C-7 may be impeded by steric or electronic factors. The addition of the salt (1c) to 2,5-dimethylaniline was examined to assess the severity of steric effects. A single product (3c), corresponding to alkylation *para* to the amine, was obtained. Even with a two-fold excess of (1c), no disubstituted products were isolated, attesting the low reactivity of the *ortho*-position. It appears that steric effects alone

would be sufficient to account for the failure of (8) to react at C-7 to produce the intermediate required for ellipticine. Other pyridocarbazoles which are unsubstituted at C-11, for example olivacine, may prove accessible by this route if conditions can be found to avoid irreversible formation of the isoquinolinium salt. Though most pyridines add irreversibly to (1a), reversible reaction with the relatively non-basic 3-cyanopyridine has been observed.[18] Further examination of the properties of quaternary salts of type (10) is required to indicate the viability of such an approach.

EXPERIMENTAL

General experimental details have been described previously.[2]

N-Alkylation of Aromatic Amines.—The amine (2.2 equiv.) was added to a stirred solution of tricarbonyl[(1,2,3,4,5-η)-cyclohexa-2,4-dienyl]iron(1+) tetrafluoroborate(1−) (1a) (200 mg) in acetonitrile (10 ml) at room temperature. After 10 min the mixture was concentrated and filtered through a short column of silica (elution with ether). The yellow band was collected. Removal of solvent and trituration with pentane gave a yellow powder which was crystallised from hexane. More product can be recovered from the filtrate by preparative t.l.c. [silica; ether–hexane 3 : 2 (v/v)].

The following compounds were prepared by the above procedure:

Tricarbonyl{N-[(2,3,4,5-η)-*cyclohexa*-2,4-*dienyl*]*benzeneamine*}*iron*(0) (2a), a yellow solid, m.p. 76—78° (Found: C, 57.6; H, 4.6; N, 4.4. $C_{15}H_{13}FeNO_3$ requires C, 57.9; H, 4.2; N, 4.5%); $\nu_{max.}$ (mull) 3 430, 1 177, 1 096, 1 063, 743, and 690 cm^{-1}; $\nu_{max.}$ (cyclohexane) 2 045 and 1 974 cm^{-1}; δ($CDCl_3$) 1.45 (1 H, dm, 6α-H), 2.27 (1 H, dq, 6β-H), 2.98 (2 H, m, NH), 3.13 (2 H, m, 2-H, 5-H), 3.92 (1 H, dt, 1β-H), 5.43 (2 H, m, 3-H, 4-H), 6.34 (2 H, m, 2′-H), 6.80 (1 H, m, 4′-H), and 7.10 (2 H, m, 3′-H); *m/z* 311 (M^+), 283, 255, 227, 225, and 219; 78% yield.

Tricarbonyl{*N*-[(2,3,4,5-η)-cyclohexa-2,4-dienyl]-4-methylbenzeneamine}iron(0) [11] (2b) a yellow solid, m.p. 99—101 °C (Found: C, 58.8; H, 4.6; N, 4.35. Calc. for $C_{16}H_{15}FeNO_3$: C, 59.1; H, 4.65; N, 4.3%); $\nu_{max.}$ (mull) 3 382, 1 180, 1 070, 940, 810, and 803 cm^{-1}; $\nu_{max.}$ (cyclohexane) 2 046 and 1 975 cm^{-1}; δ($CDCl_3$) 1.40 (1 H, d, 6α-H), 2.23 (3 H, s, CH_3), 2.39 (1 H, m, 6β-H), 3.00 (1 H, m, NH), 3.22 (2 H, m, 2-H, 5-H), 3.96 (1 H, dt, 1β-H), 5.44 (2 H, m, 3-H, 4-H), and 6.46 and 6.98 (4 H, AB system, *J* 8.5 Hz, 2′-H and 3′-H, respectively); *m/z* 325 (M^+), 297, 269, 241, 239, and 219; 69% yield. Spectroscopic properties agree well with literature [11] values.

Tricarbonyl{N-[(2,3,4,5-η)-*cyclohexa*-2,4-*dienyl*]-4-*methoxybenzeneamine*}*iron*(0) (2c), a yellow solid, m.p. 85—86 °C (Found: C, 56.45; H, 4.6; N, 4.1. $C_{16}H_{15}FeNO$ requires C, 56.35; H, 4.45; N, 4.1%); $\nu_{max.}$ (mull) 3 380, 1 031, and 818 cm^{-1}; $\nu_{max.}$ (cyclohexane) 2 047 and 1 977 cm^{-1}; δ(CCl_4) 1.38 (1 H, dm, 6α-H), 2.36 (1 H, dq, 6β-H), 2.94 (2 H, m, 5-H, NH), 3.20 (1 H, m, 2-H), 3.64 (3 H, s, OCH_3), 3.88 (1 H, dt, 1β-H), 5.30 (1 H, t, 4-H), 5.51 (1 H, t, 3-H), and 6.33 and 6.61 (4 H, AB system, *J* 9 Hz, aromatic CH); *m/z* 341 (M^+), 313, 285, 257, 255, and 219; 64% yield.

Tricarbonyl{N-[(2,3,4,5-η)-*cyclohexa*-2,4-*dienyl*]-4-*nitrobenzeneamine*}*iron*(0) (2d) was prepared by a different procedure. The salt (1a) (310 mg) was added to a solution of 4-nitroaniline in acetonitrile (3 ml). The mixture was warmed on a steam-bath for 10 min, cooled to 40 °C, and diluted slowly with water until slightly turbid. More water (3 ml) and, after 10 min at room temperature, aqueous methanol [6 ml; 1 : 1 (v/v)] were added once crystallisation had begun. After 2 h the product was collected and crystallised from ethanol as yellow plates (280 mg, 77%), m.p. 142—144 °C (Found: C, 50.45; H, 3.5; N, 7.95. $C_{15}H_{12}FeN_2O_5$ requires C, 50.6; H, 3.4; N, 7.9%); $\nu_{max.}$ (KBr) 3 356, 2 063, 1 990, 1 970, and 1 640 cm^{-1}; $\nu_{max.}$ (cyclohexane) 2 048 and 1 980 cm^{-1}; δ($CDCl_3$) 1.46 (1 H, dm, 6α-H), 2.50 (1 H, dq, 6β-H), 3.06 (1 H, m, 5-H), 3.14 (1 H, m, 2-H), 4.05 (1 H, m, 1β-H), 4.49 (1 H, d, NH), 5.42 and 5.61 (1 H, t and 1 H, t, 3-H, 4-H), 6.43 (2 H, d, 2′-H), and 8.06 (2 H, d, 3′-H); *m/z* 356 (M^+), 328, 300, 298, 272, 270, and 240.

C-Alkylation of Aromatic Amines.—A solution of the tricarbonyl(η^5-cyclohexadienyl)iron(1+) salt (1a), (1b), or (1c) (750 mg) in acetonitrile (40 ml) was added dropwise to the amine (2.2 equiv.) in acetonitrile (30 ml) at 65—70 °C. After stirring for 30 min the solution was evaporated and the excess of amine removed at 10^{-3} mmHg. The residue was extracted with boiling hexane. The crude products from the hexane extract were separated by preparative t.l.c. on silica.

The following compounds were prepared by the above procedure:

Tricarbonyl{2-[(2,3,4,5-η)-cyclohexa-2,4-dienyl]benzeneamine}iron(0) (4a), a yellow solid, m.p. 78—80 °C (Found: C, 58.1; H, 4.25; N, 4.6. Calc. for $C_{15}H_{13}FeNO_3$; C, 57.9; H, 4.2; N, 4.5%); $\nu_{max.}$ (mull 3 370, 3 450, and 754 cm^{-1}; $\nu_{max.}$ (cyclohexane) 2 045 and 1 976 cm^{-1}; δ(CCl_4) 1.53 (1 H, dm, 6α-H), 2.32 (1 H, dq, 6β-H), 3.11 (2 H, m, 2-H, 5-H), 3.20 (2 H, m, NH_2), 3.32 (1 H, dt, 1β-H), 5.42 (2 H, m, 3-H, 4-H), 6.40 (1 H, d, 6′-H), 6.57 (1 H, t, 4′-H), 6.85 (1 H, t, 5′-H), and 6.97 (1 H, d, 3′-H); *m/z* 311 (M^+), 283, 255, 227, and 225; 39% yield, was eluted [ether–hexane 1 : 4 (v/v)] ahead of tricarbonyl{4-[(2,3,4,5-η)-cyclohexa-2,4-dienyl]benzeneamine}iron(0) (3a), a yellow solid, m.p. 61—63 °C (Found: 57.4; H, 4.4; N, 4.5. Calc. for $C_{15}H_{13}FeNO_3$: C, 57.9; H, 4.2; N, 4.5%); $\nu_{max.}$ (mull) 3 480, 3 392, and 819 cm^{-1}; $\nu_{max.}$ (cyclohexane) 2 043, 1 976, and 1 972 cm^{-1}; δ(CCl_4) 1.56 (1 H, d, 6α-H), 2.31 (1 H, dq, 6β-H), 3.14 (2 H, m, 2-H, 5-H), 3.18 (1 H, m, 1β-H), 3.36 (2 H, m, NH), 5.42 (2 H, m, 3-H, 4-H), and 6.39 and 6.77 (4 H, AB system, *J* 9 Hz, aromatic CH); *m/z* 311 (M^+), 281, 255, 227, and 225; 29% yield.

Tricarbonyl{2-[(2,3,4,5-η)-4-*methoxycyclohexa*-2,4-*dienyl*]-*benzeneamine*}*iron*(0) (4e), a yellow gum (Found: C, 56.15; H, 4.45. $C_{16}H_{15}FeNO_4$ requires C, 56.35; H, 4.45%); $\nu_{max.}$ (film) 3 460, 3 370, and 745 cm^{-1}; $\nu_{max.}$ (cyclohexane) 2 042 and 1 972 cm^{-1}; δ(CCl_4) 1.65 (1 H, dt, 6α-H), 2.33 (1 H, dq, 6β-H), 2.68 (1 H, dd, 2-H), 3.10 (1 H, dt, 1β-H), 3.34 (3 H, m, NH_2, 5-H), 3.61 (3 H, s, OCH_3), 5.17 (1 H, dd, 3-H), 6.41 (1 H, dd, 6′-H), 6.59 (1 H, td, 4′-H), 6.85 (1 H, td, 5′-H), and 6.98 (1 H, dd, 3′-H); *m/z* 341 (M^+), 313, 285, 257, and 255; 41% yield, was eluted [ethyl acetate–hexane 1 : 4 (v/v)] ahead of *tricarbonyl*{4-[(2,3,4,5-η)-4-*methoxycyclohexa*-2,4-*dienyl*]*benzeneamine*}*iron*(0) (3b), a yellow solid, m.p. 92—93 °C (Found: C, 57.2; H, 4.65; N, 4.25. $C_{16}H_{15}FeNO_4$ requires C, 56.35; H, 4.45; N, 4.1%); $\nu_{max.}$ (mull 3 490, 3 395, and 823 cm^{-1}; $\nu_{max.}$ (cyclohexane) 2 041 and 1 970 cm^{-1}; δ(CCl_4) 1.65 (1 H, ddd, 6α-H), 2.29 (1 H, dq, 6β-H), 2.66 (1 H, dd, 4-H), 3.02 (1 H, dt, 1β-H), 3.33 (2 H, m, NH_2), 3.40 (1 H, m, 5-H), 3.62 (3 H, s, OCH_3), 5.05 (1 H, dd, 3-H), and 6.40 and 6.71 (4 H, AB system, *J* 8.5 Hz,

aromatic CH); *m/z* 341 (M^+), 313, 285, 257, and 255; 27% yield.

Tricarbonyl{4-[(2,3,4,5-η)-*cyclohexa*-2,4-*dienyl*]-2,5-*dimethylbenzeneamine*}*iron*(0) (3c), yellow prisms, m.p. 92—94° (Found: C, 60.15; H, 5.05; N, 4.0. $C_{17}H_{17}FeNO_3$ requires C, 60.2; H, 5.05; N, 4.15%); $\nu_{max.}$ (mull 3 460, 3 370, 795, 760, and 690 cm^{-1}; $\nu_{max.}$ (cyclohexane) 2 042 and 1 975 cm^{-1}; δ($CDCl_3$) 1.48 (1 H, dm, 6α-H), 2.08 (3 H, s, CH_3), 2.14 (3 H, s, CH_3), 2.32 (1 H, dq, 6β-H), 3.14 (2 H, m, 2-H, 5-H), 3.40 (2 H, m, NH_2), 3.50 (1 H, dt, 1β-H), 5.48 (2 H, m, 3-H, 4-H), 6.37 (1 H, s, 6'-H), and 6.82 (1 H, s, 3'-H); *m/z* 339 (M^+), 311, 283, 255, 253, 240, 197, and 163; 81% yield, was the only product. The same compound was obtained when the reaction was repeated with a two-fold excess of (1c).

Hexacarbonyl{2,6-*bis*-[(2,3,4,5-η)-*cyclohexa*-2,4-*dienyl*]-4-*methoxybenzeneamine*}*di-iron*(0) (5c); yellow needles, m.p. 138—140 °C (Found: C, 54.55; H, 4.0; N, 2.65. $C_{25}H_{21}Fe_2NO_7$ requires C, 53.7; H, 3.8; N, 2.5%); $\nu_{max.}$ (mull) 3 455, 3 385, 860, and 840 cm^{-1}; $\nu_{max.}$ (cyclohexane) 2 042 and 1 973 cm^{-1}; δ(CCl_4) 1.50 (2 H, d, 6α-H), 2.32 (2 H, dq, 6β-H), 3.10 (4 H, m, 2-H, 5-H), 3.1—3.4 (2 H, m, NH_2), 3.34 (2 H, dt, 1β-H), 3.66 (3 H, s, OCH_3), 5.48 (4 H, m, 3-H, 4-H), and 6.43 (2 H, d, 3'-H); *m/z* 559 (M^+), 531, 503, 475, 473, 445, 417, 415, 389, and 387; 6% yield, was eluted [ethyl acetate–hexane 1 : 4 (v/v)] ahead of *tricarbonyl*{2-[(2,3,4,5-η)-*cyclohexa*-2,4-*dienyl*]-4-*methoxybenzeneamine*}-*iron*(0) (4c), a yellow solid, m.p. 64—65 °C (Found: C, 55.9; H, 4.8; N, 4.1. $C_{16}H_{15}FeNO_4$ requires C, 56.35; H, 4.45; N, 4.1%); $\nu_{max.}$ (mull) 3 425, 3 360, 868, 810, and 732 cm^{-1}; $\nu_{max.}$ (cyclohexane) 2 045 and 1 974 cm^{-1}; δ($CDCl_3$) 1.58 (1 H, d, 6α-H), 2.39 (1 H, dq, 6β-H), 3.17 (2 H, m, 2-H, 5-H), 3.29 (2 H, m, NH_2), 3.41 (1 H, dt, 1β-H), 3.73 (3 H, s, OCH_3), 5.51 (2 H, m, 3-H, 4-H), and 6.56 and 6.73 (3 H, d and t, respectively, aromatic CH); *m/z* 341 (M^+), 313, 285, 257, and 255; 45% yield.

Hexacarbonyl{2,6-*bis*-[(2,3,4,5-η)-4-*methoxycyclohexa*-2,4-*dienyl*]-4-*methylbenzeneamine*}*di-iron*(0) (5d), a yellow solid, m.p. 74—75 °C (Found: C, 54.6; H, 4.1; N, 2.6. $C_{27}H_{15}Fe_2NO_7$ requires C, 53.75; H, 4.15; N, 2.3%); $\nu_{max.}$ (cyclohexane) 3 480, 3 400, 2 041, 1 972, 787, and 765 cm^{-1}; δ(CCl_4) 1.60 (2 H, d, 6α-H), 2.19 (3 H, s, CH_3), 2.33 (2 H, dq, 6β-H), 2.68 (2 H, q, 2-H), 3.10 (2 H, dt, 1β-H), 3.22 (2 H, m, NH_2), 3.38 (2 H, m, 5-H), 3.65 (6 H, s, OCH_3), 5.22 (2 H, dt, 3-H), and 6.61 (2 H, d, 3'-H); *m/z* 603 (M^+), 575, 547, 519, 517, 489, 487, 461, 459, and 431; 7% yield, was eluted [ethyl acetate–hexane 1 : 4 (v/v)] ahead of *tricarbonyl*{2-[(2,3,4,5-η)-4-*methoxycyclohexa*-2,4-*dienyl*]-4 *methylbenzeneamine*}*iron*(0) (4d), a yellow solid, m.p. 97—98 °C (Found: C, 57.5; H, 4.85; N, 4.1. $C_{17}H_{17}FeNO_4$ requires C, 57.5; H, 4.8; N, 3.95%); $\nu_{max.}$ (mull 3 439, 3 363, 820, 754, and 680 cm^{-1}; $\nu_{max.}$ (cyclohexane) 2 041 and 2 971 cm^{-1}; δ(CCl_4) 1.62 (1 H, dm, 6α-H), 2.18 (3 H, s, CH_3), 2.31 (1 H, dq, 6β-H), 2.68 (1 H, q, 2-H), 3.10 (1 H, dt, 1β-H), 3.20 (2 H, m, NH_2), 3.36 (1 H, m, 5-H), 3.62 (3 H, s, OCH_3), 5.18 (1 H, dd, 3-H), 6.31 (1 H, d, 6'-H), 6.65 (1 H, dm, 5'-H), and 6.73 (1 H, m, 3'-H); *m/z* 355 (M^+), 327, 299, 271, 269; 62% yield.

C-*Alkylation of Doubly-activated Aromatic Amines*.—A solution of the amine (1.5 equiv.) in acetonitrile (5 ml) was added to tricarbonyl[(1,2,3,4,5-η)-cyclohexa-2,4-dienyl]iron-(1+) tetrafluoroborate(1−) (1a) (200 mg) dissolved in acetonitrile (10 ml). After stirring at room temperature for 10 min the solvent was removed and the residue extracted with boiling hexane or ether. The crude product was crystallised from hexane.

The following compounds were prepared by the above procedure:

Hexacarbonyl{2,4-*bis*-[(2,3,4,5-η)-*cyclohexa*-2,4-*dienyl*]-5-*methoxybenzeneamine*}*di-iron*(0) (6a), a yellow solid, m.p. 98—99 °C [Found (for diacetate): C, 54.3; H, 4.1; N, 2.4. $C_{29}H_{25}Fe_2NO_9$ requires C, 54.15; H, 3.9; N, 2.2%]; $\nu_{max.}$ (mull) 3 480, 3 390, and 908 cm^{-1}; $\nu_{max.}$ (cyclohexane) 2 040 and 1 974 cm^{-1}; δ(CCl_4) 1.58 (2 H, d, 6α-H), 2.33 (2 H, t, 6β-H), 3.15 (4 H, m, 2-H, 5-H), 3.36 (2 H, m, NH_2), 3.57 (2 H, dt, 1β-H), 3.67 (3 H, s, OCH_3), 5.50 (4 H, m, 3-H, 4-H), 5.88 (1 H, s, 6'-H), and 6.76 (1 H, d, 3'-H); *m/z* 559 (M^+), 531, 503, 475, 473, 417, 389, 361, 343, and 341; 62% yield.

Hexacarbonyl{2,4-*bis*-[(2,3,4,5-η)-*cyclohexa*-2,4-*dienyl*]-5-*aminobenzeneamine*}*di-iron*(0) (6b), a yellow solid, m.p. 136—138 °C (Found: C, 53.15; H, 3.85; N, 5.2. $C_{24}H_{20}Fe_2N_2O_6$ requires C, 53.0; H, 3.7; N, 5.15%); $\nu_{max.}$ (mull) 3 460, 3 360, 3 330, 3 210, 979, 841, and 718 cm^{-1}; $\nu_{max.}$ (cyclohexane) 2 042 and 1 972 cm^{-1}; δ(CCl_4) 1.54 (2 H, d, 6α-H), 2.29 (2 H, dq, 6β-H), 3.0—3.4 (10 H, m, NH_2, 1β-H, 2-H, 5-H), 5.50 (4 H, m, 3-H, 4-H), 5.64 (1 H, s, 6'-H), and 6.65 (1 H, d, 3'-H); *m/z* 544 (M^+), 488, 460, 458, 400, and 372; 72% yield.

Modified C-Alkylation Procedure.—*Tricarbonyl*{2-[(2,3,4,5-η)-3-*methylcyclohexa*-2,4-*dienyl*]-4-*methylbenzeneamine*}*iron*-(0). Tricarbonyl[(1,2,3,4,5-η)-3-methylcyclohexa-2,4-dienyl]iron(1+) hexafluorophosphate(1−) (600 mg, 1.6 mmol) was added in portions to a stirred solution of ethanolic ethoxide [freshly prepared *in situ* from sodium wire (30 mg, 1.25 mmol) and ethanol (50 ml)]. *p*-Toluidine (127 mg, 1.2 mmol) was added and the mixture heated at reflux for 1 h. Glacial acetic acid (3 ml) was added and heating continued for 15 h. After cooling and addition of water, the mixture was extracted with ether. The extracts were washed with water, dried ($MgSO_4$), and evaporated to give a crude product which was purified by preparative t.l.c. [silica; ether–hexane 1 : 1 (v/v)]. Crystallisation from hexane gave yellow *needles*, m.p. 126—128 °C (Found: C, 60.6; H, 5.12; N, 4.2. $C_{17}H_{17}FeNO_3$ requires C, 60.2; H, 5.05; N, 4.15%); $\nu_{max.}$ (mull) 3 450, 3 375, 980, 810, and 715 cm^{-1}; $\nu_{max.}$ (cyclohexane) 2 043 and 1 972 cm^{-1}; δ(CCl_4) 1.50 (1 H, d, 6α-H), 2.18 (6 H, s, CH_3 and aromatic CH_3), 2.27 (1 H, dq, 6β-H), 2.98 (1 H, dq, 5-H), 3.12 (1 H, q, 2-H), 3.27 (2 H, m, NH_2), 3.34 (1 H, dt, 1β-H), 5.40 (1 H, d, 4-H), 6.34 (1 H, d, 6'-H), 6.63 (1 H, m, 3'-H), and 6.69 (1 H, dm, 5'-H); *m/z* 339 (M^+), 311, 283, 255, and 253; 80% yield based on *p*-toluidine.

Tricarbonyl{2-[(2,3,4,5-η)-*cyclohexa*-2,4-*dienyl*[-6-*amino*-5,8-*dimethylisoquinolinium*(1+)}*iron*(0) *Hexafluorophosphate*(1−) (10).—Tricarbonyl{(1,2,3,4,5-η)-cyclohexa-2,4-dienyl}iron(1+) hexafluorophosphate(1−) (1c) (211 mg, 0.58 mmol) dissolved in acetonitrile (4 ml) was added to 6-amino-5,8-dimethylisoquinoline (8) (99 mg, 0.58 mmol) suspended in acetonitrile (1 ml) at 5 °C. The isoquinoline dissolved. After stirring for 5 min the solvent was evaporated off. The crude product was washed with dry ether and dried (KOH) at 0.1 mmHg to give a fine yellow *powder* (279 mg, 90%), m.p. >330 °C (decomp.); $\nu_{max.}$ (mull 3 505, 3 404, 840, and 818 cm^{-1}; $\nu_{max.}$ (CH_3CN) 2 055 and 1 984 cm^{-1}; δ(CD_3CN) 1.78 (1 H, dm, 6α-H), 2.24 (3 H, s, 5'-CH_3), 2.62 (3 H, s, 8'-CH_3), 2.86 (1 H, dq, 6β-H), 3.12 (1 H, m, 2-H), 3.28 (1 H, m, 5-H), 5.20 (1 H, dt, 1β-H), 5.74 (2 H, m, NH_2), 5.86 (2 H, m, 3-H, 4-H), 7.14 (1 H, br, s, 7'-H), 7.89 (2 H, AB system, 3'-H, 4'-H), 8.87 (1 H, d, *J* 1 Hz, 1'-H). A portion of the product was recrystallised from acetonitrile–ethanol and washed with a small volume of cold ethanol

(Found: C, 44.9; H, 3.8; N, 5.1. $C_{20}H_{19}F_6FeN_2O_3P$ requires C, 44.8; H, 3.55; N, 5.2%)

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