Enamine Chemistry. Part 23.[1] Synthesis, Spectral Properties, and Relative Stabilities of Cyclic Dienamine Complexes of Tricarbonyliron

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Reaction of $[Fe(CO)_5]$ and the morpholine and pyrrolidine dienamines of 3,5,5-trimethylcyclohex-2-en-1-one gives a mixture of two tricarbonyl(dienamine)iron complexes. The complex in which the dienamine system is cross-conjugated has been shown to be more stable than that in which the dienamine is linearly conjugated. The reason for this, and the effect on the spectral properties, are discussed.

It is well known that the physical and chemical properties of a diene or arene are markedly affected by complex formation with a transition-metal atom. Whether the metal atom is acting in an overall electron-donating or electron-withdrawing capacity appears to depend on the property being studied.[2] However, Pettit concluded[2] that the overall electronic effect of the tricarbonyliron group appears to be one of electron donation to a diene ligand. This being the case, the stability of a diene–transition-metal complex should be significantly affected by the presence and the position of electron-donating or -withdrawing substituents in the ligand. Although complexes have previously been reported containing electron-withdrawing[3,4] and electron-donating substituents,[5,6] the relative stabilities of these complexes

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[1] Part 22, M. G. Ahmed and P. W. Hickmott, *J.C.S. Perkin II*, 1977, 838.

[2] R. Pettit, *Ann. New York Acad. Sci.*, 1965, **125**, 89.

[3] R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nuclear Chem.*, 1961, **16**, 233.

[4] M. Cais and M. Maoz, *J. Organometallic Chem.*, 1966, **5**, 370.

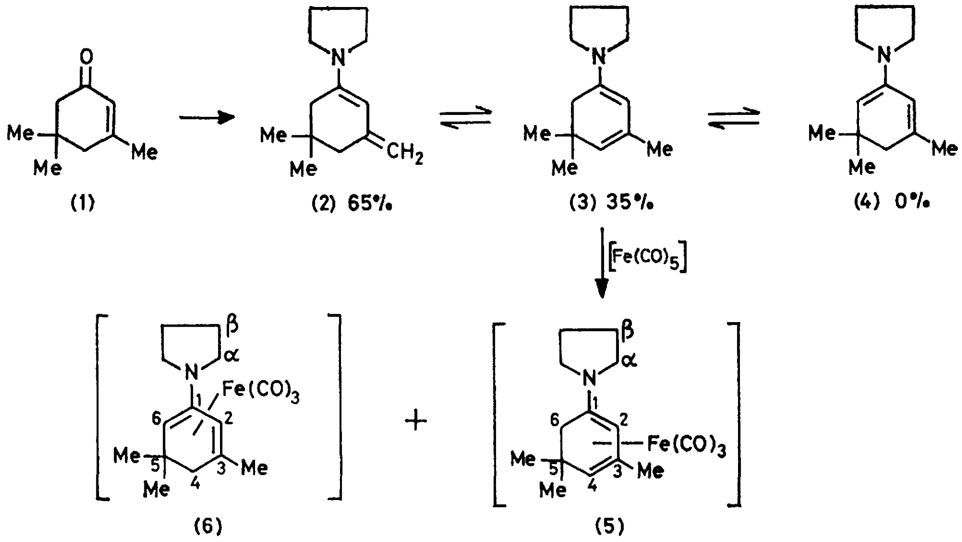
[5] A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc. (A)*, 1968, 332.

[6] R. E. Ireland, G. G. Brown, R. H. Stanford, and T. C. McKenzie, *J. Org. Chem.*, 1974, **39**, 51.

do not seem to have been evaluated. The object of this preliminary investigation was to ascertain the effect of a more strongly electron-donating substituent than has been hitherto incorporated into a diene–metal complex, namely the pyrrolidine substituent, on the stability and spectroscopic properties of the resulting complex.

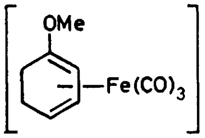
RESULTS AND DISCUSSION

We treated the pyrrolidine dienamines (2) and (3) of 3,5,5-trimethylcyclohex-2-en-1-one with pentacarbonyliron under the conditions developed by Cais and Maoz.[4] A mixture of two dienamine tricarbonyliron complexes was obtained and identified (see below) as the linearly conjugated (5) and the cross-conjugated (6). This is interesting in that our previous studies [7] have shown that the free cross-conjugated isomer (4) is not present to a detectable extent in the mixture of dienamines obtained (Scheme 1). The two complexes were separated by column chromatography and preparative t.l.c., (6) being almost colourless and relatively stable whereas (5) is yellow and very unstable, at ambient temperatures. The separation must be carried out as rapidly as possible in order to isolate complex (5) in appreciable yield. In fact the more stable isomer (6) could readily be isolated by allowing the mixture of the two isomers in pentane to stand over silica for 24 h. The less-stable isomer (5) decomposed and the decomposition products were removed by the silica. Isomer (5) could however be stored for limited periods in the dark and in the absence of air at 0 °C without too much decomposition.



Scheme 1

The greater reactivity of the linearly conjugated isomer (5) was further illustrated by treatment of the mixture of isomers with reagents normally used to liberate diene ligands from metal complexes, such as iron(III) and cerium(IV) salts. These oxidising agents rapidly removed the isomer (5), as shown by the disappearance of the metal-carbonyl stretching absorptions in the i.r. spectra of the mixture at 2 020, 1 950, and 1 940 cm^{-1}. The corresponding bands due to isomer (6) at 2 030, 1 960, and 1 952 cm^{-1} were still present after 24 h in contact with aqueous iron(III) chloride. However, no bands due to the liberated dienamine (3) were observed in the i.r. spectrum, presumably due to oxidation and hydrolysis. Similarly reaction of the mixture of isomers with the dienophile 1-phenyltriazoline-2,5-dione, which Ginsburg and his co-workers [8] have shown to give Diels–Alder adducts with tetraenic propellane metal complexes with simultaneous demetallation, resulted in rapid disappearance of (5) whereas the more-stable (6) remained unaffected. A black solid was precipitated from which no pure product could readily be separated. A similar situation appertains to the tricarbonyl(methoxycyclohexadiene)iron complexes investigated by Birch *et al.*[5] The linearly-conjugated isomer (7) was readily demetallated by manganese dioxide whereas the cross-conjugated isomer (8) was unaffected.[5] Also, as in the case of (7) and (8), we observed no evidence for the interconversion of the dienamine complexes (5) and (6) once they had been formed. The formation of (6) must therefore presumably be due to complex formation of trace amounts of (4) present in the mixture of dienamines, with subsequent continuous displacement of the equilibrium until reaction is complete.



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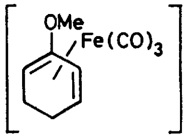

(8)

The structures of the complexes were assigned initially by comparison of their ^{1}H n.m.r. spectra with those

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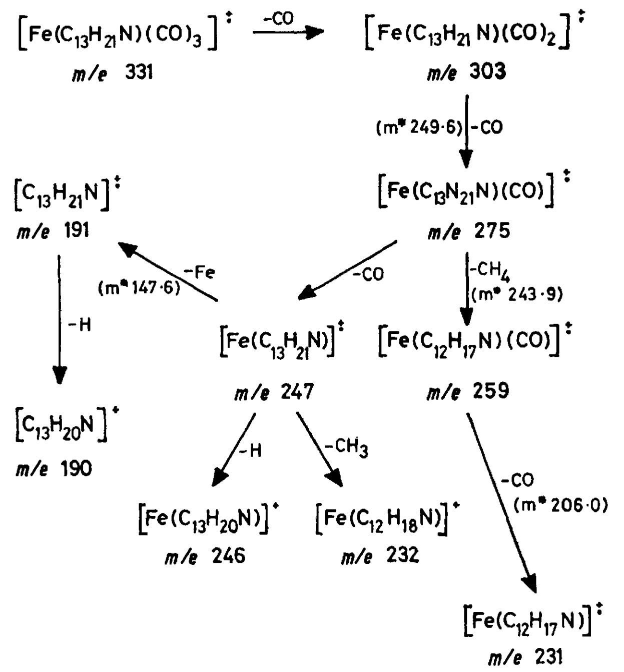
[7] N. F. Firrell and P. W. Hickmott, *J. Chem. Soc.* (*B*), 1969, 293.

[8] M. Korat, D. Tatarsky, and D. Ginsburg, *Tetrahedron*, 1972, **28**, 2315; D. Ginsburg, *Accounts Chem. Res.*, 1974, 286.

reported by Birch *et al.*[5] for methyl- and methoxy-cyclohexadiene complexes of tricarbonyliron. These structural assignments were subsequently confirmed by comparison of the i.r. and ^{13}C n.m.r. spectra with those reported by Ireland *et al.*[6] for tricarbonyl(methoxycyclohexadiene)iron complexes. Birch *et al.*[5] reported that the chemical shifts of the inner protons in cyclohexadiene complexes are virtually the same as those in the free diene, the outer or terminal protons in the complexed diene being shifted to the τ 7.0—7.5 region. This is also the case for the dienamine complexes as regards the terminal protons [H^4 of (5), τ 7.35; H^6 of (6), τ 7.2]. However, there are interesting differences as regards the inner protons. The inner proton of the linearly conjugated dienamine complex [H^2 of (5), τ 5.32] is deshielded by 0.34 p.p.m. with respect to the free dienamine.[7] More significantly, the inner proton of the cross-conjugated dienamine complex (6) (H^2, τ 5.52) is shifted by >1 p.p.m. to high field from its expected value in the free dienamine.* The implications of these observations will be discussed later. Finally, as regards the ^1H n.m.r. spectra, the chemical shift of the in-chain methyl group [in (5)] is at lower field (τ 7.85) than that of the terminal methyl group [in (6)] (τ 8.45) in agreement with previous literature assignments for analogous systems.[5]

The mass spectra of the two isomers are very similar, the main difference being in the relative stabilities of the molecular ions. Under normal operating conditions of the mass spectrometer (ion-source temperature, 200—250 °C) a weak molecular ion was observed for complex (6) but not for (5). For the purpose of accurate mass measurement the operating temperature was decreased to *ca.* 100 °C when a weak molecular ion was observed for (5) (relative abundance 2%), that for (6) also being intensified (relative abundance 15%). As in the case of tricarbonyl(cyclohexa-1,3-diene)iron [9] and ring-substituted analogues,[10] there is a sequential loss of carbon monoxide from the molecular ion to give relatively strong $[M - CO]^+$ and $[M - 2CO]^+$ ions. Unlike the fragmentation of $[Fe(C_6H_8)(CO)_3]$, which shows no $[Fe(C_6H_8)]^+$ ion, both isomers show an ion formed by loss of three CO groups but of very low abundance. A metastable transition indicates that this ion loses iron to give the dienamine molecular ion, subsequent fragmentation of which is the same as reported for the pyrrolidine enamine of 3,5,5-trimethylcyclohex-2-en-1-one.[11] The base peak, however, is formed by aromatisation of the ligand. Metastable transitions indicate that this occurs by loss of methane from the $[M - 2CO]^+$ ion, followed by loss of the remaining CO group to give $[M - 3CO - CH_4]^+$ as the base peak (Scheme 2).

The u.v. spectra of the two isomers are quite different from that of the free dienamine, which shows one intense band at 287 nm.[12] The cross-conjugated isomer (6) shows intense absorption below 220 nm and a weak shoulder at 315 nm, whereas the less-stable isomer (5) additionally shows weak but distinct peaks at 267 and 315 nm, and a weak shoulder at 400 nm. The i.r. spectra of the two isomers show three bands in the metal-carbonyl stretching region and differ in that those of (5) occur at lower wavenumber (2 020, 1 950, and 1 940 cm^{-1}) than the corresponding absorptions of (6) (2 030, 1 960, and 1 952 cm^{-1}). Similar differences have been reported by Ireland *et al.*[6] in their work on tricarbonyl(methoxycyclohexadiene)iron complexes. The less-stable [5] linearly conjugated isomer (7) gives carbonyl absorption bands at 2 030 and 1 960 cm^{-1}, whereas the more-stable [5] cross-conjugated isomer (8) gives bands at 2 045 and 1 975 cm^{-1}. Comparison with the reported values for butadienetricarbonyliron [13] (2 053, 1 985, and 1 975 cm^{-1}) and tricarbonyl(hexa-2,4-dienoic acid)iron [4] (2 100 and 2 050 cm^{-1}) indicates a transition to lower frequency as the electron-donating power of the substituent increases, the effect being greater when the substituent is linearly rather than cross-conjugated to the diene system.



SCHEME 2

In order to check the generality of these observations we also prepared the corresponding complexes from the morpholine dienamines of 3,5,5-trimethylcyclohex-2-en-1-one. A mixture of the linearly-conjugated (9) and cross-conjugated complexes (10) was again obtained, but in this case their R_F values were too similar to allow separation, and it was therefore not possible to assign

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* The chemical shift for the inner olefinic proton of the corresponding free morpholine and piperidine cross-conjugated dienamines is τ 4.38.[7]

[9] R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, 1965, **69**, 3198.

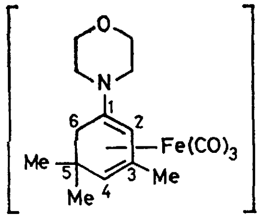
[10] M. A. Haas and J. M. Wilson, *J. Chem. Soc.* (*B*), 1968, 104.

[11] P. W. Hickmott and C. T. Yoxall, *J.C.S. Perkin II*, 1972, 890.

[12] N. F. Firrell, P. W. Hickmott, and B. J. Hopkins, *J. Chem. Soc.* (*B*), 1971, 351.

[13] K. Noack, *Helv. Chim. Acta*, 1962, **45**, 1847.

the metal-carbonyl stretching absorptions with absolute certainty. However, the lower stability of one isomer, presumably (9), was demonstrated by treatment of the mixture with anhydrous $FeCl_3$. The metal-carbonyl stretching absorptions at 2 027 and 1 955 cm^{-1} were rapidly removed from the i.r. spectrum of the mixture in pentane, and the intensity of the band at 1 960 cm^{-1} decreased.



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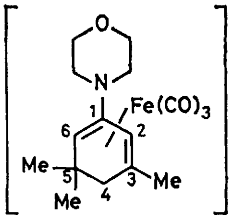

(10)

The ^1H n.m.r. spectra of the morpholine complexes (9) and (10) showed similar differences to those of the free dienamines as did the pyrrolidine complexes (5) and (6). Thus the inner proton of the linearly-conjugated complex [H^2 of (9), τ 4.82] was deshielded by 0.43 p.p.m., whereas the inner proton of the cross-conjugated complex [H^2 of (10), τ 5.28] was shifted 0.9 p.p.m. to high field from its position in the ^1H n.m.r. spectrum of the free dienamine.[7] From the point of view of the enamine system, these observations indicate that, as in the case of pyrrolidine complex (5), the double-bond character of the C^1–C^2 bond is being reduced in complex (9) so that the C^2 position is less ' enaminic ' (*i.e.* less subject to the influence of the nitrogen lone pair of electrons). Conversely the double-bond character of the C^1–C^2 bond is being increased in complex (10) [and (6)], so that the C^2 position is more ' enaminic '. Furthermore the H^2 signals in the cross-conjugated complexes [(6) and (10)] occur at higher field than the corresponding signals in the linearly-conjugated complexes [(5) and (9)], contrary to the situation in the free dienamines.[7]

In an attempt to obtain further information concerning the electron distribution and the hybridisation of the diene systems, we also recorded the ^{13}C n.m.r. spectra of the pyrrolidine complexes (5) and (6). The assignments are based on proton noise-decoupled and off-resonance-decoupled spectra, and on the relative intensities of the signals. Comparison was also made with reference substances reported in the literature.[6] At ambient temperature the carbonyl ligands give one signal, that of the cross-conjugated complex (6) being slightly to higher field (δ 214 p.p.m.) of the linearly conjugated isomer (5) (216.8 p.p.m.). With the exception of the olefinic carbon joined to nitrogen, the chemical shifts of the remaining olefinic carbons appear in the 65—85 p.p.m. region. Although the signals of the olefinic carbons joined to nitrogen are shifted to high field with respect to the C^1 signal of free pyrrolidine enamines [1] and dienamines [14] (135—147 p.p.m.), they remain in the normally accepted olefinic region [122.6 in (5), 125.5 p.p.m. in (6)]. Similarly the ^{13}C signal of the olefinic carbons joined to oxygen in tricarbonyl(methoxycyclohexadiene)iron complexes appears at 133—134 p.p.m.[6] In parallel with similar observations for the respective protons, the ^{13}C signal of the inner olefinic carbon of the cross-conjugated complex [*i.e.* C^2 in (6), 68.8 p.p.m.] appears at slightly higher field than that of the corresponding carbon in the linearly conjugated complex [*i.e.* C^2 in (5), 70.5 p.p.m.]. This would be expected following the argument that the double-bond character of the C^1–C^2 bond is increased in (6). The difference in ^{13}C chemical shifts is 1.7 p.p.m. This is not too far removed from 3.2 p.p.m., calculated from the difference in proton chemical shifts for H^2 in (6) and (5) (*i.e.* 0.2 p.p.m.) using the proportionality factors of 160 p.p.m. per electron for ^{13}C chemical shifts [15] and 10 p.p.m. per electron for ^1H chemical shifts,[15,16] and making the simplified assumption that the differences in proton and ^{13}C chemical shifts is solely due to differences in electron density. Also the signals of the terminal carbons in (6) [*i.e.* C^6 (65.5) and C^3 (67.3 p.p.m.)] are at higher field than the C^4 terminal carbon in (5) (70.5 p.p.m.). Possibly this also reflects the greater back donation from the metal to the diene system in (6) compared to (5) in agreement with our conclusions derived from the frequency of the metal-carbonyl stretching absorptions (see below). However, the dependence of ^{13}C shielding on average excitation energies [17] makes this a very tentative suggestion.

Finally, we determined the CH coupling constants for the olefinic carbons in the pyrrolidine complexes (5) and (6). Those for the inner and terminal positions of the linear complex (5) (*i.e.* C^2 and C^4) are very similar [$^1J(CH)$ 159 and 156 Hz] indicating that there is no appreciable difference in hybridisation of these carbon atoms. In the case of the cross-conjugated complex (6) the difference is somewhat larger [$^1J(C^6H)$ 154, $^1J(C^2H)$ 164 Hz]. If this difference was due solely to changes in hybridisation, the expression developed by Juan and Gutowsky [18] [$J(CH) = 500\alpha_{H^2}$] would indicate *ca.* 25% ($sp^2 \longrightarrow sp^3$) rehybridisation of the terminal C^6 position. Although the actual $J(CH)$ values are lower, the difference in the $J(CH)$ values is similar to that observed for the inner and terminal carbons of butadienetricarbonyliron which is regarded as being essentially sp^2 hybridised throughout.[19] In fact, part of this difference could be due to different π-electron contributions to the coupling constants.[18] We therefore conclude that, although a certain amount of rehybridisation may have occurred, this being somewhat greater at the terminal positions, extreme bonding situations in which the terminal pos-

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[14] M. G. Ahmed and P. W. Hickmott, unpublished work.

[15] H. Spiesecke and W. G. Scheider, *Tetrahedron Letters*, 1961, 468; P. C. Lauterbur, *ibid.*, p. 274.

[16] G. Frankel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, 1960, **82**, 5846.

[17] M. Karplus and J. A. Pople, *J. Chem. Phys.*, 1963, **38**, 2803; J. A. Pople, *Mol. Phys.*, 1964, **7**, 301.

[18] C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, 1962, **37**, 2198.

[19] H. L. Retcofsky, E. N. Frankel, and H. S. Gutowsky, *J. Amer. Chem. Soc.*, 1966, **88**, 2710.

itions of the diene system are regarded as being sp^3 hybridised can be ruled out. [20]

The increased stability of the cross-conjugated complexes is surprising in view of the greater thermodynamic stability of the free linearly conjugated compared to the free cross-conjugated dienamines.[7,21] However, this may well be a consequence of the lower frontier-orbital energies of 2-substituted compared to 1-substituted dienes [22] resulting in the formation of a metal–ligand molecular orbital of lower energy. Finally, it appears that the metal-carbonyl stretching absorptions can be correlated with the stability of the complexes. In both the dienamine and methoxydiene series the CO stretching frequencies of the more-stable isomers are higher than those of the less-stable isomers. This is indicative of greater back donation to the diene (and less back donation to the carbonyl groups) and, taking into consideration the lower frontier-orbital energies of dienes substituted by electron-withdrawing compared to electron-donating groups [22] (particularly for the LUMO), this suggests that the order of stability for diene complexes of tricarbonyliron should be: hexa-2,4-dienoic acid > butadiene > 2-methoxydienes > 1-methoxydienes, cross-conjugated dienamines > linearly conjugated dienamines.

EXPERIMENTAL

The ^{1}H and ^{13}C n.m.r. spectra were recorded on Varian A60 and CFT-20 spectrometers respectively. Carbon-13 chemical shifts are given in p.p.m. relative to $SiMe_4$. Ultraviolet spectra were recorded on a Unicam SP 800 spectrophotometer for solutions in pentane, and the i.r. and mass spectra on a Perkin-Elmer model 257 grating spectrophotometer and Atlas CH_4 or Varian MAT-711 mass spectrometers.

Preparations.—*Tricarbonyl*[η-3,5,5-*trimethyl*-1-(*pyrrolidin*-1-*yl*)*cyclohexa*-1,3-*diene*]*iron* (5) *and tricarbonyl*[η-3,5,5-*trimethyl*-1-(*pyrrolidin*-1-*yl*)*cyclohexa*-2,6-*diene*]*iron* (6). Pentacarbonyliron (8 cm^3) was added to the pyrrolidine enamine of 3,5,5-trimethylcyclohex-2-en-1-one (5.62 g) in deoxygenated peroxide-free dibutyl ether (100 cm^3) at 80 °C under dry oxygen-free nitrogen. The solution was shielded from light and heated under reflux for 3 h. The mixture was cooled, filtered from the black pyrophoric residue under nitrogen, and the solvent was removed *in vacuo*. The residue was dissolved in pentane and passed through a column of silica gel, under nitrogen and eluting with pentane. The separation was monitored by means of i.r. spectroscopy. A yellow band and the fraction showing strong metal-carbonyl absorption in the 2 000 cm^{-1} region, but devoid of ketone and dienamine absorption in the 1 600—1 700 cm^{-1} region, were combined and evaporated to dryness to give 6.64 g (68%) of a mixture of (5) and (6). This was stored at 0 °C in the dark until a pure sample was required. Purification was then effected by preparative t.l.c. on silica, eluting with pentane. This operation was performed as rapidly as possible, the chromatographic tanks again being protected from direct light. The strong reddish yellow band which separated from the base-line decomposition products was rapidly scraped off the plate, the leading edge being discarded, and extracted with pentane, filtered, and evaporated to dryness to give a pure sample of (5): M^+, 331.087 2 ($C_{16}H_{21}FeNO_3$ requires M^+, 331.087 0); *m/e* (%) 303(17), 275(10), 259(3), 247(0.5), 246(1), 232(15), 231(100), 191(25), and 190(8); τ ($CDCl_3$) 5.32(bs) (H^2), 6.95(m) (α-CH_2), 7.35(bs) (H^4), 7.85(s) (C^3–Me), 8.18(m) (β-CH_2 and H^6), 8.85(s) and 8.95(s) (C^5–Me); ^{13}C n.m.r. spectrum in C_6H_6 δ 216.8(s) (carbonyl on iron), 122.6(s) (C^1), 85.0(s) (C^3), 70.5(dd) (C^2 and C^4), 48.6(t) (α-CH_2), 44.9(t) (C^6), 35.4(q) and 31.2(q) (C^5–Me), 33.0(s) (C^5), 24.7(t) (β-CH_2), and 23.7(q) p.p.m. (C^3–Me); i.r. spectrum in pentane 2 020, 1 950, and 1 940 cm^{-1} (symmetrical and asymmetrical carbonyl stretch on iron ligands). The low stability precluded the possibility of elemental analysis.

The second band was almost colourless, but a faint yellow tinge appeared as the solvent evaporated off. This band was scraped off the plate just above the strong yellow band and, after extraction with pentane, gave a pure sample of (6): M^+, 331.087 2 ($C_{16}H_{21}FeNO_3$ requires M^+, 331.087 0); *m/e* (%) 303(15), 275(12), 259(3), 247(0.5), 246(2), 232(5), 231(100), 191(20), and 190(6); τ ($CDCl_3$) 8.45(s) (C^3–Me), 5.52(d) (*J* 2 Hz, H^2), 7.0(m) (α-CH_2), 7.2(d) (*J* 2 Hz, H^6), 8.2(m) (β-CH_2 and H^4), 8.9(s) and 9.0(s) (C^5–Me); ^{13}C n.m.r. spectrum in C_6H_6 δ 214.1(s) (carbonyl on iron), 125.5(s) (C^1), 68.8(d) (C^2), 67.3(s) (C^3), 65.5(d) (C^6), 50.0(t) (C^4), 47.6(t) (α-CH_2), 36.1(s) (C^5), 35.4(q) and 31.0(q) (C^5–Me), 26.1(q) (C^3–Me), and 24.9(t) p.p.m. (β-CH_2); i.r. spectrum in pentane 2 030, 1 960, and 1 952 cm^{-1} (symmetrical and asymmetrical carbonyl stretch on iron ligands).

Tricarbonyl(η-3,5,5-*trimethyl*-1-*morpholinocyclohexa*-1,3-*diene*)*iron* (9) *and tricarbonyl*(η-3,5,5-*trimethyl*-1-*morpholinocyclohexa*-2,6-*diene*)*iron* (10). The procedure was the same as above. Treatment of the morpholine enamine of 3,5,5-trimethylcyclohex-2-en-1-one [23] (2.74 g) with [$Fe(CO)_5$] (4 cm^3) gave 2.62 g (57%) of a mixture of (9) and (10) which could not be separated by preparative t.l.c. The relevant spectroscopic data obtained for the mixture are as follows: τ($CDCl_3$) 4.82(bs) [H^2 of (9)], 5.28(d) [*J* 2 Hz, H^2 of (10)], 6.28(m) (β-CH_2), 7.2(m) [α-CH_2 and H^4 of (9), and H^6 of (10)], 7.9(s) [C^3–Me of (9)], 8.48(s) [C^3–Me of (10)], 8.95(s) and 9.05(s) [CMe_2]; i.r. spectrum in pentane 2 032, 2 027, 1 965, 1 960, and 1 955 cm^{-1} (symmetrical and asymmetrical carbonyl stretch on iron ligands); mass spectrum, M^+ 347.

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[20] A. J. Pearson, *Austral. J. Chem.*, 1976, **29**, 1679; N. S. Nametkin, S. P. Gubin, A. I. Nekhaev, and V. D. Tyurin, *J. Organometallic Chem.*, 1976, **114**, 299.

[21] N. F. Firrell and P. W. Hickmott, *J. Chem. Soc.* (*C*), 1970, 716.

[22] K. M. Houk, *J. Amer. Chem. Soc.*, 1973, **95**, 4092.

[23] H. Nozaki, T. Yamaguti, S. Ueda, and K. Kondo, *Tetrahedron*, 1968, **24**, 1445.