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Conversion of (2-methyl-1-azabuta-1,3-diene)tricarbonyliron(0) complexes into tertiary (enamine)tricarbonyliron(0) complexes

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Abstract

Treatment of (2-methyl-1-azabuta-1,3-diene)tricarbonyliron(0) complexes with lithium diethylamide followed by a methyl iodide, benzyl bromide or allyl bromide quench leads to the formation of tertiary (enamine)tricarbonyliron(0) complexes in good yield. The crystal structures of two complexes, (2-(*N*-methyl-*N*-(4-methoxyphenyl)amino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (**19**) and (2-(*N*-allyl-*N*-isopropylamino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (**24**) are reported.

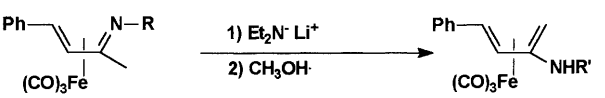
Keywords: 1-Azabuta-,3-diene; Iron; Enamine tricarbonyliron

1. Introduction

During our investigations of the reaction between (2-methyl-1-azabuta-1,3-diene)tricarbonyliron(0) complexes and lithiated amines we demonstrated that for complexes **1**–**4**, which contain a methyl group at C-2, the reaction leads to deprotonation, followed by rearrangement of the intermediate anion and consequently yields secondary (2-amino homo-1,3-diene)tricarbonyliron(0) complexes **5**–**8** in good yield [1,2] (Scheme 1).

We have also illustrated that when the substituent at C-2 of the coordinated 1-azabuta-1,3-diene is an ethyl group complexes **9**–**10** rearrange in a stereospecific manner to exclusively yield the *endo* enamine complexes **11**–**12** [3]. The stereochemistry of complexes (**11**) and (**12**) was assigned by a combination of ^{1}H-NMR and nOe difference spectroscopy (Scheme 2). In this work, nOe difference spectroscopy was used to demonstrate that the stereochemical outcome of these rearrangements was probably due to a conformationally constrained ethyl group at C-2 of the coordinated 1-azabuta-1,3-diene complexes **9** and **10** [3].

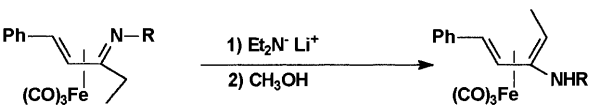
In this paper, we report that this rearrangement reaction can be used for the synthesis of tertiary enamine complexes. Although tertiary enamine complexes in the cyclohexa-1,3-diene series have been previously synthesised [4] our deprotonation strategy represents the first synthesis of acyclic tertiary (enamine)-tricarbonyliron(0) complexes (Table 1).



(1) R = C_6H_5
(2) R = $C_6H_5CH_2$
(3) R = 4-MeO-C_6H_4
(4) R = $(CH_3)_2CH$

(5) R = C_6H_5
(6) R = $C_6H_5CH_2$
(7) R = 4-MeO-C_6H_4
(8) R = $(CH_3)_2CH$

Scheme 1.



(9) R = Ph
(10) R = $PhCH_2$

(11) R = Ph
(12) R = $PhCH_2$

Scheme 2.

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Table 1
Synthesis of tertiary (enamine)tricarbonyliron(0) complexes from (1-azabuta-1,3-diene)tricarbonyliron(0) complexes

Entry	1-Azabuta-1,3-diene complex	Alkylating agent	Tertiary enamine complex	Yield (%)
1	**1**	CH_3I	**13**	82
2	**1**	$C_6H_5CH_2Br$	**14**	46
3	**1**	$H_2C{=}CHCH_2Br$	**15**	68
4	**2**	CH_3I	**16**	58
5	**2**	$C_6H_5CH_2Br$	**17**	76
6	**2**	$H_2C{=}CHCH_2Br$	**18**	82
7	**3**	CH_3I	**19**	46
8	**3**	$C_6H_5CH_2Br$	**20**	54
9	**3**	$H_2C{=}CHCH_2Br$	**21**	66
10	**4**	CH_3I	**22**	64
11	**4**	$C_6H_5CH_2Br$	**23**	48
12	**4**	$H_2C{=}CHCH_2Br$	**24**	72

2. Results and discussion

Initially the reaction between lithium diethylamide and complex **1** followed by a methyl iodide quench was studied. A solution of complex **1** in tetrahydrofuran was added to a solution of lithium diethylamide in THF at 0°C and the reaction was stirred for 3 h under an atmosphere of nitrogen. An excess of methyl iodide was added and the reaction was stirred for a further 0.5 h whilst warming up to room temperature (r.t.). Filtration of the reaction mixture following chromatography led to the isolation of a yellow oil, which crystallised on standing to yield yellow crystals identified from their spectroscopic and analytical data as complex **13**.

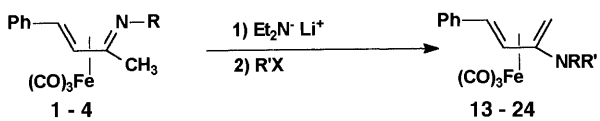
The applicability of this reaction was also studied using benzyl bromide and allyl bromide as quenchers for the rearranged intermediates derived from complexes **1**–**4**. Incorporation of an allyl group at nitrogen has allowed a useful reactive functionality to be introduced onto these enamine complexes, and hence, expand their potential application in organic synthesis (Scheme 3).

All attempts to generate the tertiary enamine complexes **13**–**24** by treatment of secondary enamine complexes **5**–**8** with alkylating agents in the presence of a mild base failed and only the starting complexes **1**–**4** were obtained. When lithiated secondary enamine complexes, generated by the reaction of complexes **5**–**8** with butyl-lithium, were quenched with alkylating agents the reactions lead to the formation of tertiary enamine complexes in acceptable yields. It appears therefore that these tertiary enamine complexes are only accessible by alkylation of the lithiated enamine complexes by either quenching the rearrangement of 1-azabuta-1,3-diene complexes, or the anion generated by reaction of secondary enamine complexes with butyl-lithium (Scheme 4).

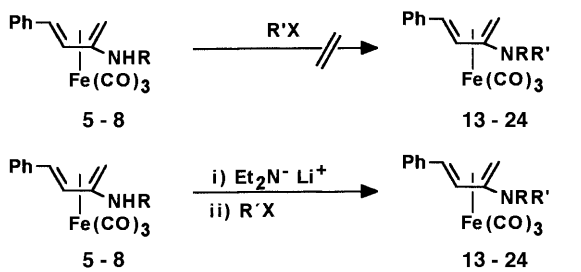
Crystal structures of complexes **19** (Fig. 1) and **24** (Fig. 2) were obtained. Relevant data is summarised in Table 2.

Complex **19** has a monoclinic unit cell containing eight molecular units. The iron atom is bound to three carbonyl ligands and is approximately equidistant from each of the carbon atoms comprising the buta-1,3-diene fragment. The buta-1,3-diene fragment itself shows a dihedral angle of 7.66° between C(4) and C(7) and may be considered as approximately planar as in (buta-1,3-diene)tricarbonyliron(0) [6]. The minor deviation from planarity is attributed to the substituents at C(7) and C(5). The dihedral angle C(6)–C(7)–C(11)–C(10) (6.33°) indicates that the phenyl substituent at C(7) is essentially co-planar to the buta-1,3-diene fragment. In the case of the substituents at nitrogen the methyl is slightly below the plane of the buta-1,3-diene fragment and the 4-methoxy phenyl group shows a pronounced twist along the N(1)–C(21) bond. Selected bond lengths, bond angles and dihedral angles for this complex are shown in Tables 3–5.

For complex **24** the unit cell is again monoclinic and in this case contains four molecular units. A similar arrangement of the buta-1,3-diene and carbonyl ligands to those described for complex **19** exists. The dihedral angle C(4)–C(5)–C(6)–C(7) in this case is 13.48°. The C(8) of the allyl fragment is below the buta-1,3-diene



Scheme 3.



Scheme 4.

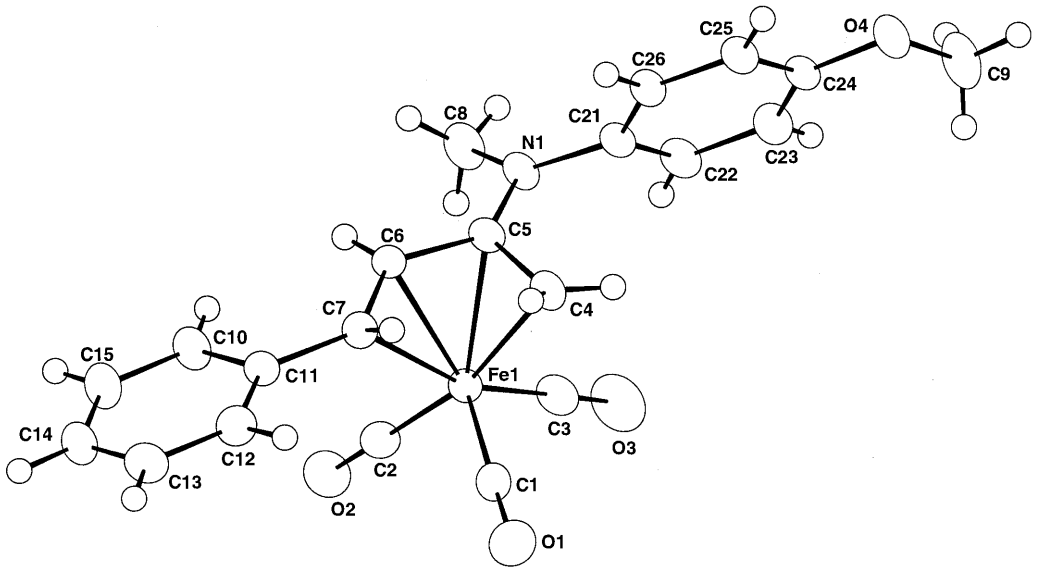


Fig. 1. Crystal structure of (2-(*N*-methyl-*N*-(4-methoxyphenyl)amino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (**19**).

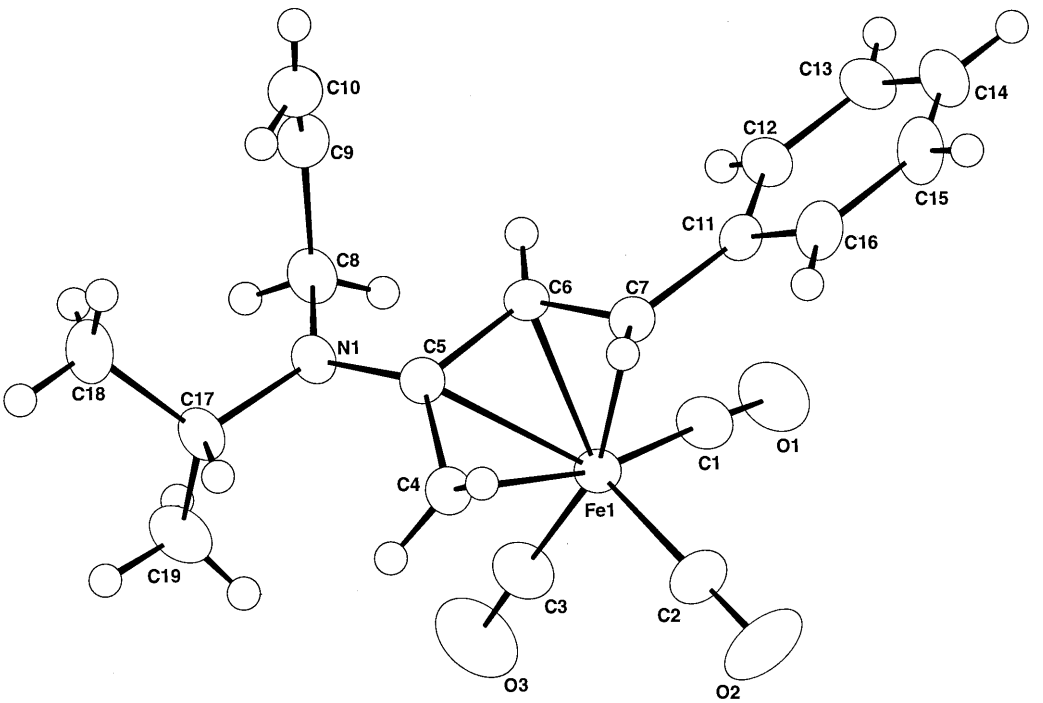


Fig. 2. Crystal structure of (2-(*N*-allyl-*N*-isopropylamino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (**24**).

whilst C(9) and C(10) of the alkene fragment is above. The methine carbon of the isopropyl fragment is approximately in the plane of the buta-1,3-diene while the methyl groups are orientated above and below the plane of the buta-1,3-diene fragment. The phenyl group at C(7) shows similar behaviour to that observed for complex **19**. Selected bond lengths, bond angles and dihedral angles for complex **24** are shown in Tables 6–8.

In both complexes **19** and **24** one of the hydrogens at C(4) [H(42)] is situated over the tricarbonyliron(0) moiety and explains the high chemical shift observed for these atoms in the ^{1}H-NMR spectrum [5].

In both complexes the Fe–C and C–O bond lengths associated with the carbonyl groups are approximately equal and characteristic of those expected for a (buta-1,3-diene)tricarbonyliron(0) complex [6]. Also, for complexes **19** and **24** the nitrogen atoms at C(2) are

approximately planar and the C(2)–N(1) bond lengths are 1.367 and 1.373 Å, respectively. This is consistent with the presence of a planar sp^2 nitrogen bound to an sp^2 carbon [7] and suggests a degree of delocalisation into the buta-1,3-diene fragment.

Table 2
Crystallographic data for complexes **19** and **24**

	Complex **19**	Complex **24**
Empirical formula	$C_{21}H_{19}NFeO_4$	$C_{19}H_{21}NFeO_3$
Formula weight	405.23	367.23
Temperature (K)	293	293
Wavelength (Å)	0.71069	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
a (Å)	23.005	17.132
b (Å)	7.909	8.470
c (Å)	21.285	12.699
α (°)	90	90
β (°)	90	90
γ (°)	97.93	93.86
Volume (Å^3)	3835.6	1838.5
Z	8	4
D_{calc} (g cm^{-3})	1.396	1.327
Absorption coefficient (cm^{-1})	8.0	8.3
$F(000)$	1536	768
Crystal size (mm^3)	$0.4\times0.4\times0.15$	$0.3\times0.3\times0.3$
Index ranges	$0\le h\le28$, $0\le k\le9$, $-26\le l\le26$	$0\le h\le21$, $0\le k\le10$, $-15\le l\le15$
Reflections collected	4140	3999
Independent reflections $I>\sigma3(I)$	2902	2850
Refinement method [a]	FMLSSF	FMLSSF
Data/restraints/parameters		
Goodness-of-fit on F^2	1.059	1.095
$R(F)$	0.0339	0.0337
$wR(F^2)$	0.0394	0.0393

[a] FMLSSF = Full-matrix least-squares structure factors.

Table 3
Selected interatomic distances (Å) for complex **19**

Bond	Length	Bond	Length
Fe(1)–C(1)	1.79(4)	C(7)–C(6)	1.423(4)
Fe(1)–C(2)	1.797(3)	C(7)–C(11)	1.489(4)
Fe(1)–C(3)	1.787(4)	C(4)–H(41)	1.14(3)
Fe(1)–C(4)	2.104(3)	C(4)–H(42)	0.87(3)
Fe(1)–C(5)	2.170(3)	C(6)–H(6)	0.97(3)
Fe(1)–C(6)	2.077(3)	C(7)–H(7)	1.02(3)
Fe(1)–C(7)	2.119(3)	C(5)–N(1)	1.373(4)
C(5)–C(4)	1.437(5)	N(1)–C(8)	1.455(4)
C(6)–C(5)	1.429(4)	N(1)–C(21)	1.441(4)

Table 4
Selected bond angles (°) for complex **19**

Atoms	Angle	Atoms	Angle
C(1)–Fe(1)–C(2)	100.3(2)	C(6)–C(5)–C(4)	114.2(3)
C(1)–Fe(1)–C(3)	101.1(2)	C(7)–C(6)–C(5)	118.4(3)
C(2)–Fe(1)–C(3)	91.7(2)	C(5)–C(4)–H(41)	118.9(17)
C(4)–Fe(1)–C(5)	39.3(1)	C(5)–C(4)–H(42)	117.5(22)
C(5)–Fe(1)–C(6)	39.25(9)	H(41)–C(4)–H(42)	112.9(26)
C(6)–Fe(1)–C(7)	39.6(1)	C(5)–C(6)–H(6)	119.7(18)
C(5)–Fe(1)–C(7)	69.6(1)	C(7)–C(6)–H(6)	171.7(17)
C(4)–Fe(1)–C(6)	70.3(1)	C(6)–C(7)–H(7)	119.6(16)
C(7)–Fe(1)–C(4)	79.8(1)	C(6)–C(7)–C(11)	122.9(3)
Fe(1)–C(1)–O(1)	178.6(3)	C(4)–C(5)–N(1)	123.0(3)
Fe(1)–C(2)–O(2)	179.4(3)	C(6)–C(5)–N(1)	122.1(3)
Fe(1)–C(3)–O(3)	177.8(4)	C(8)–N(1)–C(21)	118.0(3)
Fe(1)–C(4)–H(42)	119.5(21)	C(5)–N(1)–C(21)	120.8(3)
Fe(1)–C(4)–H(41)	109.4(15)	C(5)–N(1)–C(8)	120.5(3)

Table 5
Selected dihedral angles for complex **19**

Bonds	Angle	Bonds	Angle
C(4)–C(5)–C(6)–C(7)	7.66	C(6)–C(5)–N(1)–C(8)	15.64
C(4)–C(5)–N(1)–C(8)	155.27	C(6)–C(7)–C(11)–C(10)	6.33
C(5)–N(1)–C(21)–C(26)	65.26	C(6)–C(7)–C(11)–C(12)	172.96
C(5)–N(1)–C(21)–C(22)	116.48		

Table 6
Selected interatomic distances (Å) for complex **24**

Bond	Length	Bond	Length
Fe(1)–C(1)	1.782(3)	C(6)–C(7)	1.422(4)
Fe(1)–C(2)	1.795(4)	C(7)–C(11)	1.476(4)
Fe(1)–C(3)	1.778(4)	C(4)–H(41)	1.00(3)
Fe(1)–C(4)	2.102(3)	C(4)–H(42)	0.90(3)
Fe(1)–C(5)	2.214(3)	C(6)–H(6)	0.90(2)
Fe(1)–C(6)	2.064(3)	C(7)–H(7)	0.86(3)
Fe(1)–C(7)	2.120(3)	N(1)–C(8)	1.454(4)
C(4)–C(5)	1.441(4)	N(1)–C(17)	1.484(4)
C(5)–C(6)	1.424(4)	N(1)–C(5)	1.367(3)

Table 7
Selected bond angles for complex **24**

Atoms	Angle	Atoms	Angle
C(1)–Fe(1)–C(2)	96.7(2)	C(4)–C(5)–C(6)	113.6(3)
C(1)–Fe(1)–C(3)	90.8(1)	C(5)–C(6)–C(7)	119.3(3)
C(2)–Fe(1)–C(3)	101.5(2)	C(5)–C(4)–H(41)	116.9(17)
C(4)–Fe(1)–C(5)	38.9(1)	C(5)–C(4)–H(42)	119.5(21)
C(5)–Fe(1)–C(6)	38.7(1)	H(41)–C(4)–H(42)	111.9(25)
C(6)–Fe(1)–C(7)	39.7(1)	C(5)–C(6)–H(6)	119.5(15)
C(4)–Fe(1)–C(6)	70.3(1)	C(7)–C(6)–H(6)	120.9(15)
C(7)–Fe(1)–C(4)	80.1(1)	C(6)–C(7)–H(7)	112.5(17)
Fe(1)–C(1)–O(1)	177.3(3)	C(4)–C(5)–N(1)	123.7(3)
Fe(1)–C(2)–O(2)	178.1(3)	C(6)–C(5)–N(1)	122.3(2)
Fe(1)–C(3)–O(3)	177.7(4)	C(8)–N(1)–C(17)	117.7(2)
Fe(1)–C(4)–H(41)	120.9(16)	C(5)–N(1)–C(17)	122.0(2)
Fe(1)–C(4)–H(42)	108.2(20)	C(5)–N(1)–C(8)	119.5(2)

Table 8
Selected dihedral angles for complex **24**

Atoms	Angle	Atoms	Angle
C(4)–C(5)–C(6)–C(7)	13.48	C(5)–N(1)–C(17)–C(19)	99.91
C(4)–C(5)–N(1)–(C8)	154.48	C(6)–C(5)–N(1)–C(17)	171.94
C(5)–N(1)–C(8)–C(9)	82.78	C(6)–C(7)–C(11)–C(12)	20.59
C(5)–N(1)–C(17)–C(18)	134.47	C(6)–C(7)–C(11)-C(16)	156.73

3. Experimental

All reactions carried out under an atmosphere of dry nitrogen were performed using standard vacuum and Schlenk line techniques [8]. Complexes **1**–**4** were synthesised in accordance with literature procedures [1,2]. Diethyl ether was dried over lithium aluminiumhydride and was distilled, toluene was dried over sodium metal and was distilled and tetrahydrofuran was dried over potassium benzophenone ketyl and was distilled. Diethylamine was redistilled and butyllithium was used as a 1.6 M solution in hexanes. Melting points were recorded on a Kofler hot-stage micro-melting point apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC 300 instrument at 300 and 75.4 MHz, respectively. All chemical shifts are quoted in parts per million relative to a tetramethylsilane standard. Flash chromatography was performed on Merck (40–63 μm) silica. IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR spectrometer. Filtrations through alumina were performed using deactivated Brockmann (grade 4) alumina. Elemental analyses were performed on a Leeman Laboratories CE 477 instrument.

4. Crystal structures

4.1. Data collection and processing

Crystal structures were determined using an Enraf–Nonius CAD4 diffractometer using graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å), Structures were solved and refined with SHELEX-87 using standard procedures [9].

For complex **19** the coordinates of the iron atom were derived from a Patterson synthesis and a subsequent F_o map revealed all but four atoms of the ligand and a subsequent structure factor/Fourier cycle produced the complete molecule. With the inclusion of hydrogen atoms in positions determined from a difference map R fell to 0.087. Anisotropic full-matrix refinement, initially with the iron atom alone and then with the remaining non-hydrogen atoms converged at $R = 3.39$, $R_w = 3.94$ and $S = 1.059$.

For complex **24** the coordinates of the iron atom were derived from a Patterson synthesis but a subsequent F_o map only revealed 19 further atoms of the ligand. Subsequent structure factor/Fourier cycles eventually produced the complete molecule. With the inclusion of hydrogen atoms in fixed calculated positions ($d_H = 1.0$ Å) R fell to 0.096. Anisotropic full-matrix refinement, initially with the iron atom alone and then with the remaining non-hydrogen atoms converged at $R = 3.37$, $R_w = 3.93$ and $S = 1.095$

4.2. (2-(N-Methyl-N-phenylamino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (**13**)

Diethylamine (0.01 g, 1.38 mmol) was added to tetrahydrofuran (5 ml) and the resulting solution was cooled to 0°C. Butyl-lithium (1.6 M, 0.88 ml, 1.40 mmol) was added and the solution was stirred at 0°C for 0.25 h under an atmosphere of nitrogen. A solution of complex **1** (0.10 g, 0.28 mmol) in tetrahydrofuran (5 ml) was added and the dark solution produced was stirred at 0°C for 3 h under an atmosphere of nitrogen. Iodomethane (0.20 g, 1.38 mmol) was added and the reaction mixture was allowed to warm up to r.t. The dark mixture produced was filtered through a plug of alumina to remove the solid residue and the solvent was removed under reduced pressure to yield a yellow gum. This gum was chromatographed on silica using 1:10 diethyl ether–hexane as the eluent to yield a yellow oil which crystallised on standing to yield yellow crystals (0.085 g, 82%). M.p. 101–102°C. Found: C, 64.02; H, 4.42; N, 3.64. $C_{20}H_{17}FeNO_3$ requires: C, 63.99; H, 4.57; N, 3.73%. IR (C_4Cl_6): ν_{max} 2038vs (C≡O) and 1973vs br cm^{-1} (C≡O). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 0.67 (1H, d, $J_{\alpha-3}$ 5.0 Hz, C=CH_β), 1.86 (1H, d, J 8.2 Hz, PhCH=CH), 2.09 (1H, dd, $J_{\alpha-3}$ 1.8 Hz and $J_{\alpha-\beta}$ 5.0 Hz, C=CH_α), 3.28 (3H, s, NCH_3), 5.19 (1H, d, J 7.7 Hz, PhCH=CH) and 7.10–7.41 (10H, m, 2 × aryl–H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 35.30 (C=CH_2), 38.70 (NCH_3), 55.15 (C4), 63.05 (C3), 124.93, 125.06, 125.77, 126.10, 127.20, 128.41, 129.45, 141.84 and 146.87 (2 × aryl–H and C2).

4.3. (N-Benzyl-N-phenylamino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (**14**)

Yellow crystals. (0.060 g, 46%). M.p. 119–121°C. Found: C, 69.14; H, 4.74; N, 2.86. $C_{26}H_{21}NFeO_3$ requires: C, 69.17; H, 4.96; N, 3.10%. IR (C_4Cl_6):

ν_{max} 2038vs (C≡O), 1973vs (C≡O) and 1961vs cm^{-1}. (C≡O)^{1}H-NMR (300 MHz; $CDCl_3$): δ 0.72 (1H, d, J 5.0 Hz, C=CH_α), 1.80 (1H, d, J 8.1 Hz, PhCH=CH), 2.14 (1H, dd, $J_{\alpha-3}$ 1.9 Hz and $J_{\alpha-\beta}$ 5.1 Hz, C=CH_α), 4.73 (1H, d, J 16.6 Hz, PhCHHN), 5.03 (1H, d, J 16.6 Hz, PhCHHN), 5.14 (1H, d, J 7.6 Hz, PhCH=CH) and 7.01–7.40 (15H, m, 3 × aryl–H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 37.17 (C=CH$_2$), 55.15 (C4), 55.90 (CH$_2$Ph), 64.29 (C3), 125.30, 125.77, 125.83, 126.05, 126.64, 127.35, 128.39, 128.84, 129.69, 138.15 and 141.71 (3 × Ph and C2).

4.4. (2-(N-Allyl-N-phenylamino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (15)

Yellow oil (0.076 g, 68%). B.p. > 100°C (dec.). Found: C, 65.55; H, 4.55; N, 3.29; $C_{22}H_{19}FeNO_3$ requires: C, 65.82; H, 4.77; N, 3.49). B.p. > 100°C (dec.) IR (thin film): ν_{max} 2034vs (C≡O) and 1958vs br cm^{-1} (C≡O). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 0.68 (1H, d, J 5.1 Hz, C=CH_β), 1.82 (1H, d, J 8.1 Hz, PhCH=CH), 2.10 (1H, dd, $J_{\alpha-3}$ 1.9 Hz and $J_{\alpha-\beta}$ 5.1 Hz, C=CH$_\alpha$), 4.15–4.43 (2H, m, NCH_2CH=CH$_2$), 5.18 (1H, d, J 7.5 Hz, PhCH=CH), 5.22–5.41 (2H, m, NCH$_2$CH=CH_2), 5.94–6.05 (1H, m, NCH$_2$CH=CH$_2$) and 7.07–7.42 (10H, m, 2 × aryl–H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 36.01 (C=CH$_2$), 54.52 (NCH$_2$CH=CH$_2$), 55.07 (C4), 63.58 (C3), 117.03 (NCH$_2$CH=CH$_2$), 125.46, 125.75, 126.05, 126.10, 127.56, 128.41, 129.61, 133.69, 141.93 and 145.92 (2 × Ph, C2 and NCH$_2$CH=CH$_2$).

4.5. (2-(N-Methyl-N-benzylamino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (16)

Yellow crystals, (0.061 g, 58%). M.p. 78–79°C. Found: C, 64.63; H, 4.79; N, 3.59% $C_{21}H_{19}NFeO_3$ requires: C, 64.77; H, 4.92; N, 3.60%. IR (C_4Cl_6): ν_{max} 2037s (C≡O), 1972s (C≡O) and 1955s cm^{-1} (C≡O).^{1}H-NMR (300 MHz; $CDCl_3$): δ 0.49 (1H, d, J 5.2 Hz, C=CH_β), 1.84 (1H, d, J 8.0 Hz, PhCH=CH), 2.20 (1H, dd, $J_{\alpha-3}$ 2.0 Hz and $J_{\alpha-\beta}$ 5.1 Hz, C=CH), 2.85 (3H, s, NCH_3), 4.23 (1H, d, J 15.8 Hz, PhCHHN), 4.35 (1H, d, J 15.8 Hz, PhCHHN), 5.12 (1H, d, J 7.2 Hz, PhCH=CH) and 7.09–7.39 (10H, m, 2 × aryl–H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 31.61 (C=CH$_2$), 38.27 (NCH$_3$), 55.33 (C4), 56.38 (NCH$_2$Ph), 61.65 (C3), 125.66, 126.08, 127.24, 127.50, 128.38, 128.81, 129.44, 137.56 and 142.09 (2 × Ph and C2).

4.6. (2-(N,N-Dibenzylamino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (17)

Yellow oil, (0.094 g, 76%). M.p. > 100°C (dec.) .Found: C, 69.44; H, 4.80; N, 3.00; $C_{27}H_{23}NFeO_3$ requires: C, 69.66, H 4.98; N, 3.01. IR (thin film): ν_{max} 2033vs (C≡O) and 1942vs br cm^{-1} (C≡O). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 0.48 (1H, d, J 5.4 Hz, C=CH_β), 1.79 (1H, d, J 8.0 Hz, PhCH=CH), 2.21 (1H, dd, $J_{\alpha-3}$ 1.9 Hz and $J_{\alpha-\beta}$ 5.3 Hz, C=CH_α), 4.33 (2H, d, J 15.9 Hz, 2 × PhCHHN), 4.51 (2H, d, J 15.9 Hz, 2 × PhCHHN), 5.19 (1H, d, J 7.4 Hz, PhCH=CH) and 7.05–7.38 (15H, m, 3 × aryl–H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 32.80 (C=CH$_2$), 55.31 (C4), 55.38 (2 × PhCH$_2$), 63.53 (C3), 125.69, 126.03, 127.48, 127.53, 128.39, 128.72 and 137.36 (3 × Ph and C2).

4.7. (2-(N-(Allyl)-N-benzylamino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (18)

Yellow oil (0.083 g, 82%). B.p. > 120°C (dec.). Found: C, 66.40; H, 4.99; N, 3.25% $C_{23}H_{21}FeNO_3$ requires: C, 66.49; H, 5.10; N, 3.37%. IR (thin film): ν_{max} 2034s (C≡O), 1966s (C≡O) and 1959s cm^{-1} (C≡O). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 0.48 (1H, d, J 5.3 Hz, C=CH_β), 1.80 (1H, d, J 8.0 Hz, PhCH=CH), 2.22 (1H, dd, $J_{\beta-3}$ 1.9 Hz and $J_{\alpha-\beta}$ 5.3 Hz, C=CH_α), 3.86 (2H, m, NCH_2CH=CH$_2$), 4.27 (1H, d, J 16.3 Hz, PhCHHN), 4.45 (1H, d, J 16.3 Hz, PhCHHN), 5.11 (1H, d, J 7.4 Hz, PhCH=CH), 5.26 (2H, m, NCH$_2$CH=CH_2), 5.91 (1H, m, NCH$_2$CH=CH$_2$) and 7.10–7.50 (10H, m, 2 × aryl–H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 31.93 (C=CH$_2$), 54.01 (NCH$_2$Ph and NCH$_2$CH=CH$_2$), 55.19 (C4), 62.15 (C3), 118.27 (NCH$_2$CH=CH_2), 125.65, 126.07, 127.07, 127.42, 128.38, 128.80, 129.79, 133.25, 137.62 and 142.12 (2 × Ph, C2 and NCH$_2$CH=CH$_2$).

4.8. (2-(N-Methyl-N-(4-methoxyphenyl)amino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (19)

Yellow crystals, (0.048 g, 46%). M.p. 124–126°C. Found: C, 62.10; H, 4.56; N, 3.45%, $C_{21}H_{19}NFeO_4$ requires: C, 62.24; H, 4.73; N, 3.45%. IR (C_4Cl_6): ν_{max} 2036vs (C≡O), 1971vs (C≡O) and 1954vs cm^{-1} (C≡O). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 0.55 (1H, d, J 5.2 Hz, C=CH_β), 1.85 (1H, d, J 8.2 Hz, PhCH=CH), 2.02 (1H, dd, $J_{\alpha-3}$ 1.9 Hz and $J_{\alpha-\beta}$ 5.1 Hz, C=CH_α), 3.20 (3H, s, NCH_3), 3.83 (3H, s,OCH_3), 5.05 (1H, d, J 7.6 Hz, PhCH=CH) and 6.93–7.23 (9H, m, 2 × aryl–H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 32.68 (C=CH$_2$), 39.25 (NCH$_3$), 55.36 (C4), 55.46 (OCH$_3$), 62.18 (C3), 114.77, 125.66, 126.07, 126.95, 128.35, 128.83, 139.33, 142.00 and 57.51 (2 × Ph and C2).

4.9. (2-(N-Benzyl-N-(4-methoxyphenyl)amino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (20)

Yellow oil, (0.068 g, 54%). B.p. > 100°C (dec.). Found: C, 67.20: H, 4.87; N, 2.80. $C_{27}H_{23}FeNO_4$ requires: C, 67.35; H, 4.82: N, 2.91%. IR (thin film): ν_{max} 2034vs (C≡O) and 1967vs, br cm^{-1} (C≡O)^{1}H-NMR (300 MHz; $CDCl_3$): δ 0.60 (1H, d, J 5.2 Hz, C=CH_β),

1.80 (1H, d, J 8.1 Hz, PhCH=CH), 2.06 (1H, dd, $J_{\alpha-3}$ 1.8 Hz and $J_{\alpha-\beta}$ 5.2 Hz, C=CH_{α}), 3.80 (3H, s,OCH_3), 4.63 (1H, d, J 16.2 Hz, PhCHHN), 4.88 (1H, d, J 16.2 Hz, PhCHHN), 5.02 (1H, d, J 7.7 Hz, PhCH=CH) and 6.70–7.38 (15H, m, 3 × aryl–H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 34.81 (C=CH$_2$), 55.34 (C4), 55.42 (OCH$_3$), 56.37 (NCH$_2$Ph), 63.30 (C3), 114.92, 125.86, 126.04, 126.92, 127.33, 127.97, 128.31, 129.09, 137.99, 141.76 and 141.90 (3 × Ph and C2).

4.10. (2-(N-Allyl-N-(4-methoxyphenyl)amino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (21)

Yellow oil, (0.075 g, 66%). B.p. > 100°C (dec.). Found: C, 63.80; H, 5.01; N, 3.10. $C_{23}H_{21}FeNO_4$ requires: C, 64.02; H, 4.91; N, 3.25%. IR (thin film): ν_{max} 2036s (C≡O), 1971s (C≡O) and 1956s cm^{-1} (C≡O)^{1}H-NMR (300 MHz; $CDCl_3$): δ 0.57 (1H, d, J 5.2 Hz, C=CH_{β}), 1.81 (1H, d, J 8.1 Hz, PhCH=CH), 2.03 (1H, dd, $J_{\alpha-3}$ 1.8 Hz and $J_{\alpha-\beta}$ 5.2 Hz, C=CH_{α}), 3.84 (3H, S,OCH_3), 4.06–4.29 (2H, m, NCH_2CH=CH$_2$), 5.03 (1H, d, J 7.7 Hz, PhCH=CH), 5.20–5.36 (2H, m, NCH$_2$CH=CH_2), 5.93–6.02 (1H, m, NCH$_2$CH=CH$_2$) and 6.93–7.26 (9H, m, 2 × aryl–H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 33.63 (C=CH$_2$), 55.07 (NCH$_2$CH=CH$_2$), 55.23 (C4), 55.45 (OCH$_3$), 62.48 (C3), 117.12 (NCH$_2$CH=CH_2), 114.88, 125.64, 126.08, 128.19, 128.36, 129.13, 133.60, 138.22 and 142.10 (2 × Ph, C2 and NCH$_2$CH=CH$_2$).

4.11. (2-(N-Methyl-N-isopropylamino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (22)

Yellow oil, (0.066 g, 64%). B.p. > 100°C (dec.). Found C, 59.60; H, 5.75; N, 3.99. $C_{17}H_{19}FeNO_3$ requires: C, 59.81; H, 5.61 N, 4.11%. IR (C_4Cl_6): ν_{max} 2035vs (C≡O), 1969vs (C≡O) and 1954vs cm^{-1} (C≡O). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 0.44 (1H, d, J 5.2 Hz, C=CH$_{\beta}$), 1.19 (6H, d, J 6.6 Hz, CH(CH_3)$_2$), 1.85 (1H, d, J 7.9 Hz, PhCH=CH), 2.15 (1H, dd, $J_{\alpha-3}$ 2.0 Hz and $J_{\alpha-\beta}$ 5.3 Hz, C=CH_{α}), 2.73 (3H, s, NCH$_3$), 4.04 (1H, sept, J 6.6 Hz, CH(CH$_3$)$_2$), 5.04 (1H, d, J 7.1 Hz, PhCH=CH) and 7.08–7.26 (5H, m, aryl–H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 19.31 and 19.64 (CH(CH$_3$)$_2$), 29.75 (NCH$_3$), 30.71 (C=CH$_2$), 49.75 (CH(CH$_3$)$_2$), 54.84 (C4), 58.50 (C3), 125.46, 125.56, 126.06, 128.33, 131.74 and 142.69 (Ph and C2).

4.12. (2-(N-Benzyl-N-isopropylamino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (23)

Yellow oil, (0.034 g, 48%). B.p. > 100°C (dec.). IR (C_4Cl_6): ν_{max} 2037vs (C≡O), 1971vs (C≡O) and 1957vs cm^{-1} (C≡O). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 0.50 (1H, d, J 4.9 Hz,C=CH_{β}), 1.27 (3H, d, J 6.3 Hz,CH(CH_3)$_2$), 1.32 (3H, d, J 6.3 Hz, CH(CH_3)$_2$), 1.80 (1H, dd, $J_{\alpha-3}$ 1.7 Hz and $J_{\alpha-\beta}$ 4.9 Hz,C=CH_{α}), 1.85 (1H, d, J 7.9 Hz, PhCH=CH), 3.26–3.63 (2H, m, PhCH_2N), 5.13 (1H, d, J 7.9 Hz, PhCH=CH) and 6.83–7.29 (10H, m, 2 × aryl–H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 22.22 and 23.90 (CH(CH$_3$)$_2$), 29.69 (CH(CH$_3$)$_2$), 30.87 (C=CH$_2$), 44.89 (NCH$_2$Ph), 54.54 (C4), 60.68 (C3), 125.57, 126.04, 128.29, 128.38, 128.59 and 128.90 (2 × Ph and C2).

4.13. (2-(N-Allyl-N-isopropylamino)-4-phenylbuta-1,3-diene)tricarbonyliron(0) (24)

Yellow crystals (0.045 g, 72%). M.p. 95–96°C. Found: C, 62.11; H, 5.78; N, 3.73%$C_{19}H_{21}NFeO_3$ requires: C, 62.14; H, 5.76; N 3.81%. IR (C_4Cl_6): ν_{max} 2034vs (C≡O), 1969vs (C≡O) and 1952vs cm^{-1} (C≡O). ^{1}H-NMR (300 MHz; $CDCl_3$): δ 0.46 (1H, d, $J_{\alpha-\beta}$5.4 Hz, C=CH_{β}), 1.16 (3H, d, J 6.7 Hz, CHCH_3), 1.22 (3H, d, J 6.7 Hz, CHCH_3), 1.83 (1H, d, J 7.9 Hz, PhCH=CH), 2.18 (1H, dd, $J_{\alpha-3}$ 1.8 Hz and $J_{\alpha-\beta}$ 5.4 Hz, C=CH_{α}), 3.73 (2H, m, NCH_2CH=CH$_2$), 4.05 (1H, sept, J 6.7 Hz, CH(CH$_3$)$_2$), 5.05 (1H, d, J 7.8 Hz, PhCH=CH), 5.30 (2H, m, NCH$_2$CH=CH_2), 5.96 (1H, m, NCH$_2$CH=CH$_2$), and 7.08–7.26 (5H, m, aryl–H). ^{13}C-NMR (75 MHz; $CDCl_3$): δ 19.53 (CHCH_3), 20.86 (CHCH_3), 31.29 (C=CH$_2$), 47.02 (NCH$_2$CH=CH$_2$), 50.26 (CH(CH$_3$)$_2$), 55.06 (C4), 59.81 (C3), 116.13 (NCH$_2$CH=CH_2), 125.48, 126.08, 128.34, 131.88, 135.96 and 142.66 (Ph, C2 and NCH$_2$CH=CH$_2$).

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 142582 for compound (**19**) and CCDC No. 142583 for compound (**24**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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