Diastereoselective Formation of Tricarbonyliron(0) Complexes of 1-Aza-1,3-dienes Bearing Chiral Substituents

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Syntheses of two series of novel 1-aza-1,3-dienes bearing chiral substituents on nitrogen [PhCH=CHCH=NCH(R)Ph (R = Et, Pr^i and Bu^t) and PhCH=CHCH=NCH(R)Me (R = Et, Pr^i and Bu^t)] are described and the stereochemical outcome of their complexation reactions with $Fe_2(CO)_9$ reported. Diastereoisomeric ratios of 93:7 and 94:6 are observed on complexation of PhCH=CHCH=NCH(Bu^t)Ph **10** and PhCH=CHCH=NCH(Bu^t)Me **19** respectively. The structures of the major diastereoisomers of **10** and **19** have been determined by NOE measurements.

As a result of our interest in the reactivity of transition metal ligands containing π-bound heteroatoms, we have recently undertaken investigations into the chemistry of tricarbonyliron(0) complexes of 1-oxa-1,3-dienes and 1-aza-1,3-dienes. We have discovered, for example, that addition of a range of hard nucleophiles to tricarbonyl(1-oxa-1,3-diene)iron(0) complexes results in the clean production of 1,4-diketones when performed under a nitrogen atmosphere[1,2] but that tricarbonyl('vinylketene')iron(0) complexes are generated when the addition is carried out under a carbon monoxide atmosphere.[3] We have also studied alkyl-lithium attack on tricarbonyl(1-aza-1,3-diene)iron(0) complexes and found that, in general, this leads to pyrrole formation under remarkably mild reaction conditions.[4,5]

During our investigations into nucleophilic attack on tricarbonyl(1-aza-1,3-diene)iron(0) complexes we synthesised tricarbonyl[1-(α-methylbenzyl)-4-phenyl-1-azabuta-1,3-diene]-iron(0) **1** and found that it was formed as a 1:1 mixture of diastereoisomers.[5] NOE experiments in conjunction with molecular modelling studies enabled us to determine that the preferred conformations of the two diastereoisomers **1a** and **1b** are those shown in Fig. 1. The aim of the study described below was to increase the diastereoselectivity of the complexation reaction by altering the structure of the amine used to generate the 1-aza-1,3-diene. It was envisaged that examination of the effect of 1-aza-1,3-diene substituent structure on the diastereoselectivity of complexation would allow us to identify factors which lead to good diastereoselectivity in this particular complexation, and that this information could then be used in future to achieve high selectivity in other systems which involve interactions between nitrogen atoms bearing chiral substituents and metal species.[6]

Results and Discussion

Initially it was of interest to examine the effect of increasing the steric bulk of the alkyl group on the diastereoselectivity of the complexation reaction, and thus 1-aza-1,3-dienes **2**, **3** and **4** were synthesised as follows. 1-Phenylpropylamine **5**, 2-methyl-1-phenylpropylamine **6** and 2,2-dimethyl-1-phenylpropylamine **7**, formed from the appropriate ketone *via* the Leuckart reaction,[7] were condensed with cinnamaldehyde to give the novel 1-aza-1,3-dienes **2**, **3** and **4** (identified on the basis of their analytical, ^{1}H NMR, ^{13}C NMR, IR and MS data) in 64, 80 and 80% yield respectively.

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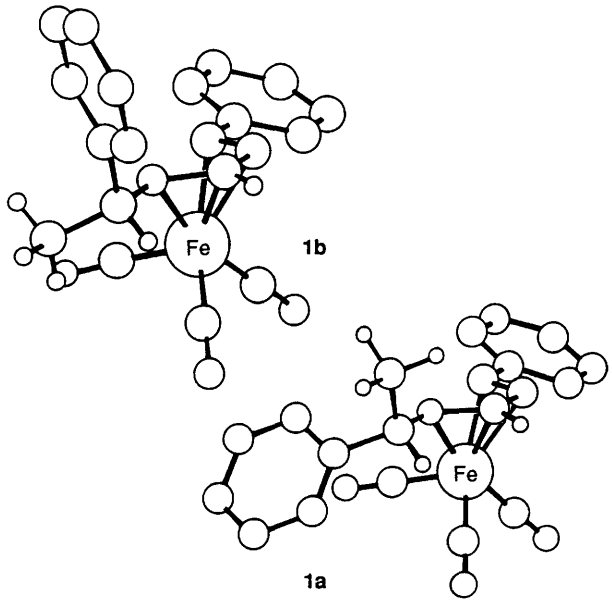
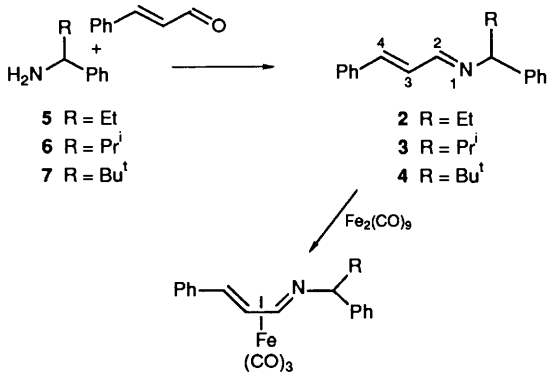


Fig. 1 Diastereoisomers of complex **1**, [Fe(CO$_3$){PhCH(Me)N=CHCH=CHPh}], in their most stable conformations as predicted by CHEM-X and supported by NOE experiments[5]

The 1-aza-1,3-dienes **2**, **3** and **4** were then heated with an equimolar amount of $Fe_2(CO)_9$ at 50–60 °C for 1.5–2 h to complex them to the tricarbonyliron(0) moiety. Filtration and concentration of the dark brown reaction mixtures gave brown residues from which yellow–orange products were isolated by column chromatography. The products were identified as diastereoisomeric mixtures of the novel tricarbonyliron(0) complexes **8** (40%), **9** (48%) and **10** (17%) on the basis of their ^{1}H NMR, IR and MS data. The ratios of diastereoisomers produced were determined from the integrals of the signals due to 2-H and 3-H of each complex and found to be 2:1, 3:1 and 93:7 for complexes **8**, **9** and **10** respectively. [Examination of the ^{1}H NMR spectra of the crude products and the corresponding purified complexes showed that chromatography had not altered the diastereoisomeric ratios of products **8**, **9** and **10**.]

The diastereoisomeric ratios obtained on complexation of the 1-aza-1,3-dienes of **2**, **3** and **4** to the tricarbonyliron(0) unit thus indicate that increasing the steric bulk of the alkyl substituent leads to higher diastereoselectivity in the complexation reaction.

Whilst the initial aim of this study (which was to increase significantly the diastereoselectivity of complexation of 1-aza-



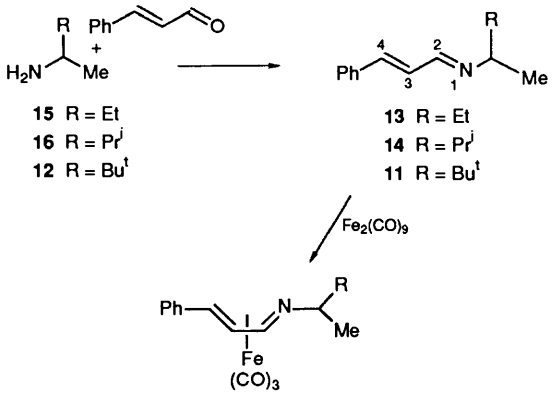
5 R = Et
6 R = Pr^i
7 R = Bu^t

2 R = Et
3 R = Pr^i
4 R = Bu^t

8 R = Et **8a** : **8b** = 2:1[a]
9 R = Pr^i **9a** : **9b** = 3:1[a]
10 R = Bu^t **10a** : **10b** = 93:7[b]

[a] Measured from 220 MHz ^{1}H NMR spectrum. [b] Measured from 400 MHz ^{1}H NMR spectrum.

1,3-dienes bearing chiral substituents adjacent to the nitrogen atom) had been achieved, the amine **7**, which ultimately led to the highest diastereoisomeric ratio on complexation, was relatively expensive and thus unattractive for potential future applications (2,2-dimethyl-1-phenylpropylamine **7** was synthesised from t-butyl phenyl ketone). It appeared that the phenyl group at the chiral centre of the 1-aza-1,3-diene could be regarded as a substituent whose effective steric bulk was intermediate between the t-butyl group and the hydrogen atom. It was reasoned that this rôle would be equally well fulfilled by a methyl substituent and so 1-(α-t-butylethyl)-4-phenyl-1-azabuta-1,3-diene **11**, derived from relatively inexpensive 2-amino-3,3-dimethylbutane **12**, was synthesised and the diastereoselectivity of its complexation reaction with $Fe_2(CO)_9$ examined. In addition, the related 1-aza-1,3-dienes **13** and **14** were also synthesised and the diastereoselectivity of their complexation reactions measured.



15 R = Et
16 R = Pr^i
12 R = Bu^t

13 R = Et
14 R = Pr^i
11 R = Bu^t

17 R = Et **17a** : **17b** = 1:1[a]
18 R = Pr^i **18a** : **18b** = 1:1[a]
19 R = Bu^t **19a** : **19b** = 94:6[b]

[a] Measured from 220 MHz ^{1}H NMR spectrum. [b] Measured from 400 MHz ^{1}H NMR spectrum.

Condensation of commercially available 2-aminobutane **15**, 2-amino-3-methylbutane **16** and 2-amino-3,3-dimethylbutane **12** with cinnamaldehyde proceeded smoothly to give the novel 1-aza-1,3-dienes **13**, **14** and **11** (characterised by their analytical, ^{1}H NMR, ^{13}C NMR, IR and MS data) in 68, 76 and 66% yield respectively.

Complexation of the 1-aza-1,3-butadienes **13**, **14** and **11** by heating with $Fe_2(CO)_9$ followed by filtration, concentration and chromatography led to the isolation of the corresponding novel tricarbonyliron(0) complexes **17**, **18** and **19** (identified by their ^{1}H NMR, IR and MS data) in 43, 56 and 28% yield respectively. The disastereoisomeric ratios were measured from the signals due to 2-H and 3-H and found to be 1:1 for complexes **17** and **18** and 94:6 for complex **19**. Thus the diastereoselectivity obtained on complexation of 1-aza-buta-1,3-diene **19**, derived from relatively inexpensive 2-amino-3,3-dimethylbutane **12**, is comparable with that obtained on complexation of 1-azabuta-1,3-diene **10**, derived from relatively expensive 2,2-dimethyl-1-phenylpropylamine **7**. With respect to future applications of 2-amino-3,3-dimethylbutane **12** to the control of carbon–nitrogen double bond interactions with metal centres or surfaces, it is of note that the amine **12** has been resolved *via* its tartrate salt.[8]

Assignment of the Relative Stereochemistry and Lowest Energy Conformations of Major Diastereoisomers.—In order to determine the structures of the major diastereoisomers of complexes **10** and **19**, formed in diastereoisomeric ratios of 93:7 and 94:6 respectively, a series of NOE experiments were performed. For the major diastereoisomer of complex **10**, *i.e.* **10a**, (i) irradiation of 2-H led to an enhancement of the signals due to 3-H (7%) and the methine proton (9%), (ii) irradiation of the methine proton led to an enhancement of the signals due to 2-H (9%) and the *ortho*-protons of the phenyl group (6%, δ 6.90; 4%, δ 7.65) and (iii) irradiation of the protons of the t-butyl group led to an enhancement of the signals due to 4-H (6%), 2-H (8%), the methine proton (12%) and the *ortho*-protons of the phenyl group (8%, δ 6.90; 8%, δ 7.65).

For the major diastereoisomer of complex **19**, *i.e.* **19a**, (i) irradiation of 2-H led to an enhancement of the signals due to 3-H (6%) and the methine proton (6%), (ii) irradiation of the methyl protons led to an enhancement of the signal due to the methine proton (5%) and (iii) irradiation of the protons of the t-butyl group led to an enhancement of the signals due to 2-H (11%), 4-H (4%) and the methine proton (19%).

The lowest energy conformations predicted for **1a** and **1b** both place the hydrogen atom at the carbon chiral centre in the same sterically encumbered area of space on the same side of the 1-aza-buta-1,3-diene plane as the tricarbonyliron(0) group. Assuming that in the related complexes **10** and **19** the methine proton will occupy this position in preference to a t-butyl group, then the observed NOE results indicate that the major diastereoisomers of **10** and **19** have the structures **10a** and **19a** (see Fig. 2).

Examination of the ^{1}H NMR shifts of 2-H and 3-H in complexes **1**, **8**, **9** and **10** reveals that 2-H and 3-H of the major diastereoisomer are found at lower field than 2-H and 3-H in the minor diastereoisomer (see Table 1). The consistency of these shifts strongly suggests that the major diastereoisomers formed in the complexation reactions of 1-azabuta-1,3-dienes **2** and **3**, *i.e.* **8a** and **9a** have the same relative stereochemistry and lowest energy conformation as diastereoisomer **10a** (see Fig. 3).

Experimental

Reactions under nitrogen were performed using standard vacuum line and Schlenk tube techniques.[9] Diethyl ether was dried over sodium wire and light petroleum refers to the fraction boiling in the range 30–40 °C. 1-Phenylpropylamine **5**, 2-methyl-1-phenylpropylamine **6** and 2,2-dimethyl-1-phenylpropylamine **7** were prepared from propiophenone, 2-methylpropiophenone, and 2,2-dimethylpropiophenone respectively *via* the Leuckart reaction,[7] and enneacarbonyldi-iron(0) was prepared from pentacarbonyliron(0) using a published procedure.[10] Chromatography was performed on SiO_2 (Merck, 40–63 μm). M.p.s were obtained on a Gallenkamp capillary m.p. apparatus and are uncorrected. Elemental analyses were

Table 1 ^{1}H NMR shifts of 2-H and 3-H in major and minor diastereoisomers of complexes, **1**, **8**, **9** and **10**

Complex	δ[a] 2-H in major diastereoisomer **a**	δ 2-H in minor diastereoisomer **b**	δ 3-H in major diastereoisomer **a**	δ 3-H in minor diastereoisomer **b**
1[b]	6.7	6.5	5.55	5.45
8	6.7	6.5	5.5	5.4
9	6.7	6.5	5.55	5.45
10	6.65	6.45	5.47	5.38

[a] ppm, $CDCl_3$, 220 MHz (**1**, **8**, **9**) or 400 MHz **10**. [b] Diastereoisomeric ratio of **1** = 1:1. 'Major' and 'minor' assigned to correlate with **8**, **9** and **10**.

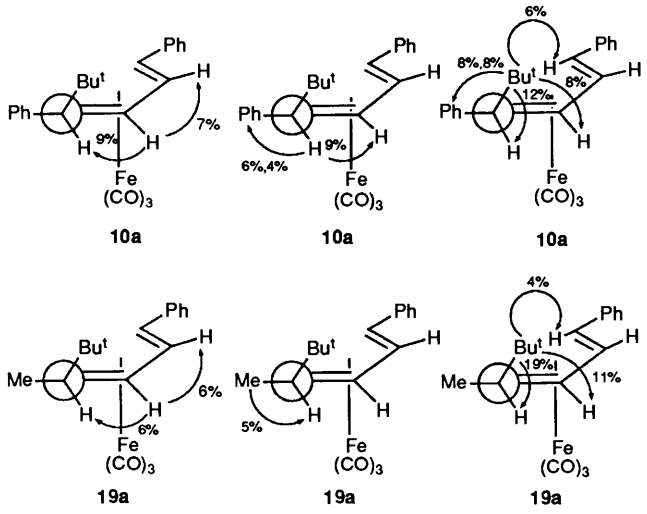


Fig. 2 NOE results obtained from the major diastereoisomers of complexes **10** and **19**. (Complexes **10a** and **19a** are represented in their proposed most stable conformation.)

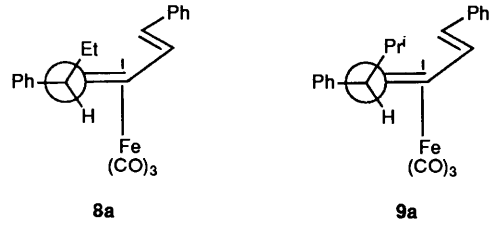


Fig. 3 Proposed lowest energy conformation of major diastereoisomers of complexes **8** and **9**

performed by Butterworth Laboratories Ltd. and MEDAC Ltd, Brunel University Chemistry Department. IR spectra were obtained on a Perkin-Elmer 580B instrument and calibrated against a polystyrene standard. NMR spectra were recorded in $CDCl_3$ on Perkin-Elmer R34 (220 MHz ^{1}H) and Bruker WH 400 (400 MHz ^{1}H, 100.6 MHz ^{13}C) spectrometers; *J* values in Hz. Mass spectra were recorded on a Kratos MS 80 instrument using EI, CI (NH_3) and FAB (matrix – *m*-nitrobenzyl alcohol[11]) techniques.

1-(α-*Ethylbenzyl*)-4-*phenyl*-1-*azabuta*-1,3-*diene* **2**.—1-Phenylpropylamine **5** (2.70 g, 0.02 mol) was added to cinnamaldehyde (2.64 g, 0.02 mol) at 0 °C and stirred for 15 min. The yellow solid produced was dissolved in diethyl ether to give a solution which was dried ($MgSO_4$), filtered, and concentrated to give yellow crystals of **2** (3.19 g, 64%), m.p. 36.8–39.6 °C (Found: C, 86.7; H, 7.7; N, 5.6. $C_{18}H_{19}N$ requires C, 86.75; H, 7.75; N, 5.65%); ν_{max}(Nujol)/cm^{-1} 1640m (C=N) and 1620w (C=C); δ_H(220 MHz) 0.85 (3 H, t, *J* 7, CH_3), 1.9 (2 H, m, CH_2), 4.05 (1 H, t *J* 7, C*H*Et), 6.9 (2 H, m, 3-H, 4-H), 7.3–7.5 (10 H, m, 2 × Ph) and 8.1 (1 H, d, *J* 9, 2-H); δ_C 10.9 (Me), 31.2 (CH_2), 77.1 (*C*HEt), 126.7, 126.9, 127.0, 128.1, 128.3, 128.6, 128.9, 135.7, 144.0 (2 × Ph and C-3), 141.5 (C-4) and 161.5 (C-2); *m*/*z* (CI): 250 (M^+ + 1, 100%) and 220 (95, M – Et).

1-(α-*Isopropylbenzyl*)-4-*phenyl*-1-*azabuta*-1,3-*diene* **3**.—2-Methyl-1-phenylpropylamine **6** (2.98 g, 0.02 mol) was added to cinnamaldehyde (2.64 g, 0.02 mol) at 0 °C and stirred for 15 min. The product was dissolved in diethyl ether and the resulting solution dried ($MgSO_4$), filtered and concentrated to give yellow crystals of the *title compound* **3** (4.23 g, 80%), m.p. 40.7–42.4 °C (Found: *m*/*z* 263.1665. $C_{19}H_{21}N$ requires 263.1674); ν_{max}(Nujol)/cm^{-1} 1640m (C=N) and 1620w (C=C); δ_H(220 MHz) 0.80 (3 H, d, *J* 7, Me), 0.95 (3 H, d, *J* 7, Me), 2.2–2.3 (1 H, m, C*H*Me$_2$), 3.75 (1 H, d, *J* 9, C*H* Pr^i), 7.0 (2 H, m, 3-H, 4-H), 7.3–7.6 (10 H, m, 2 × Ph) and 8.1 (1 H, d, *J* 9, 2-H); δ_C 19.5, 19.6 (2 × CH_3), 34.6 (*C*HMe$_2$), 83.0 (*C*HPr^i), 126.7, 126.9, 127.0, 127.5, 128.1, 128.6, 128.8, 135.7, 143.4 (2 × Ph and C-3), 141.4 (C-4) and 161.5 (C-2); *m*/*z* (CI): 264 (M^+ + 1, 56%) and 220 (100, M – Pr^i).

1-(α-t-*Butylbenzyl*)-4-*phenyl*-1-*azabuta*-1,3-*diene* **4**.—A solution of cinnamaldehyde (132 mg, 1.00 mmol) in diethyl ether (5 ml) was added to 2,2-dimethyl-1-phenylpropylamine **7** (140 mg, 0.86 mmol) at 0 °C and stirred for 15 min. After addition of further diethyl ether (5 ml), the solution was dried ($MgSO_4$), filtered and concentrated to give white crystals of the *title compound* **4** (190 mg, 80%), m.p. 127.6–129.8 °C (Found: C, 86.6; H, 8.4; N, 4.95. $C_{20}H_{23}N$ requires C, 86.59; H, 8.36; N, 5.05%); ν_{max}(Nujol)/cm^{-1} 1640m (C=N) and 1620w (C=C); δ_H(220 MHz): 0.95 (9 H, s, Bu^t), 3.9 (1 H, s, C*H* Bu^t), 7.0 (2 H, m, 3-H, 4-H), 7.3–7.5 (10 H, m, 2 × Ph) and 8.1 (1 H, d, *J* 9, 2-H); δ_C 26.9 (C(*C*H$_3$)$_3$), 35.6 [*C*(CH$_3$)$_3$], 85.7 (*C*Bu^t), 126.5, 127.1, 127.4, 128.5, 128.6, 128.78, 128.82, 135.7, 143.5 (2 × Ph and C-3), 141.3 (C-4) and 161.7 (C-2); *m*/*z* (CI): 278 (M^+ + 1, 30%) and 220 (100, M – Bu^t).

1-(α-*Ethylethyl*)-4-*phenyl*-1-*azabuta*-1,3-*diene* **13**.—2-Aminobutane **15** (1.46 g, 0.02 mol) was added to cinnamaldehyde (2.64 g, 0.02 mol) at 0 °C and the mixture stirred for 15 min. The product mixture was dissolved in diethyl ether and the resulting solution dried ($MgSO_4$), filtered and concentrated to give **13** as a yellow thermally unstable liquid (2.53 g, 68%) (Found: *m*/*z* 187.1361. $C_{13}H_{17}N$ requires 187.1361); ν_{max}(thin film)/cm^{-1} 1640m (C=N) and 1620w (C=C); δ_H(220 MHz); 0.85 (3 H, t, *J* 7, CH_2CH_3), 1.25 (3 H, d, *J* 6, $CHCH_3$), 1.6 (2 H, m, CH_2CH_3), 3.1 [1 H, m, C*H*(Me)Et], 7.0 (2 H, m, 3-H, 4-H), 7.35–7.55 (5 H, m, Ph) and 8.1 (1 H, d, *J* 6, 2-H); δ_C 10.8 (CH_2CH_3), 22.2 ($CHCH_3$), 30.6 (CH_2CH_3), 67.9 (*C*H(Me)Et), 127.1, 128.3, 128.7, 128.9, 135.8 (Ph and C-3), 141.0 (C-4) and 160.4 (C-2); *m*/*z* (EI): 187 (M^+, 24%), 172 (10, M – Me), 158 (68, M – Et) and 115 (100, C_9H_7).

1-(α-*Isopropylethyl*)-4-*phenyl*-1-*azabuta*-1,3-*diene* **14**.—2-Amino-3-methylbutane **16** (1.74 g, 0.02 mol) was added to cinnamaldehyde (2.64 g, 0.02 mol) at 0 °C and the mixture stirred for 15 min. The product mixture was dissolved in diethyl ether and the resulting solution dried ($MgSO_4$), filtered and concentrated to give **14** as an orange thermally unstable liquid (3.06 g, 76%) (Found: C, 83.45; H, 9.55; N, 6.7. $C_{14}H_{19}N$

requires C, 83.53; H, 9.51; N, 6.96%); ν_{max}(thin film)/cm^{-1} 1640m (C=N) and 1620w (C=C); δ_H(220 MHz) 0.85 [3 H, d, *J* 7, one of CH(CH_3)$_2$], 0.95 [3 H, d, *J* 7, one of CH(CH_3)$_2$], 1.2 [3 H, d, *J* 7, CH(CH_3)], 1.75 (1 H, m, C*H*Me$_2$), 2.9 [1 H, m, C*H*(Me)Pr^i], 7.0 (2 H, m, 3-H, 4-H), 7.3–7.4 (5 H, m, Ph) and 8.05 (1 H, d, *J* 7, 2-H); δ_C 19.1, 19.3, 19.8 (3 × Me), 34.1 (*C*HMe$_2$), 72.4 [*C*H(Me)Pr^i], 127.0, 128.3, 128.6, 128.8, 135.8 (Ph and C-3), 140.9 (C-4) and 160.4 (C-2); *m*/*z* (EI): 201 (M$^+$, 11%), 186 (3, M − Me), 158 (100, M − Pr^i), 115 (57, C_7H_9).

1-(α-t-*Butylethyl*)-4-*phenyl*-1-*azabuta*-1,3-*diene* **11**.—2-Amino-3,3-dimethylbutane **12** (2.02 g, 0.02 mol) was added to cinnamaldehyde (2.64 g, 0.02 mol) at 0 °C and the mixture stirred for 15 min. The yellow solid produced was dissolved in diethyl ether and the resulting solution dried ($MgSO_4$), filtered and concentrated to give yellow crystals of **11** (2.85 g, 66%), m.p. 94.8–96.7 °C (Found: C, 83.55; H, 9.8; N, 6.7. $C_{15}H_{21}N$ requires C, 83.66; H, 9.83; N, 6.50%); ν_{max}(Nujol)/cm^{-1} 1635m (C=N) and 1620w (C=C); δ_H(220 MHz): 0.9 (9 H, s, Bu^t), 1.15 (3 H, d, *J* 6, CHCH_3), 2.9 [1 H, q, *J* 6, C*H*(Me)Bu^t], 6.95 (2 H, m, 3-H, 4-H), 7.3–7.55 (5 H, m, Ph) and 8.05 (1 H, d, *J* 6, 2-H); δ_C 17.3 (CH*C*H$_3$), 26.5 [C(*C*H$_3$)$_3$], 34.1 [*C*(CH$_3$)$_3$], 75.8 [*C*H(Me)Bu^t], 127.0, 128.3, 128.7, 128.8, 135.9 (Ph and C-3), 141.0 (C-4) and 160.6 (C-2); *m*/*z* (EI): 215 (M$^+$, 6%), 200 (9, M − Me), 158 (100, M − Bu^t) and 115 (67, C_7H_9).

Tricarbonyl[1-(α-*ethylbenzyl*)-4-*phenyl*-1-*azabuta*-1,3-*diene*]*iron*(0) **8**.—Enneacarbonyldi-iron(0) (1.31 g, 3.60 mmol) and 1-(α-ethylbenzyl)-4-phenyl-1-azabuta-1,3-diene **2** (0.93 g, 3.73 mmol) were added to toluene (15 ml) and the resulting mixture maintained at 50–60 °C under nitrogen for 2 h. The red mixture produced was filtered and the solvent removed from the filtrate under reduced pressure to yield a dark red oil which was chromatographed (SiO_2; light petroleum–diethyl ether, 15:1) to yield a 2:1 mixture of **8a** and **8b** as an orange oil (0.58 g, 40%); ν_{max}(hexane)/cm^{-1} 2050vs, 1995vs and 1975vs (C≡O); δ_H(220 MHz) 0.70 and 0.75 (3 H, t, *J* 8, CH$_2$CH_3 **8b**, **8a**), 1.7–1.85 (2 H, m, CH_2CH$_3$), 2.8 (1 H, m, C*H*Et), 3.075 and 3.125 (1 H, d, *J* 10, 4-H **8a**, **8b**), 5.4 and 5.5 (1 H, dd, *J* 3 and 10, 3-H **8b**, **8a**), 6.5 and 6.7 (1 H, d, *J* 3, 2-H **8b**, **8a**) and 7.2–7.4 (10 H, m, 2 × Ph); *m*/*z* (FAB): 390 (M$^+$ + 1, 100%), 362 (8, MH − CO), 333 (43, M − 2CO), 306 (73, MH − 3CO) and 250 [28, MH − Fe(CO)$_3$].

Tricarbonyl[1-(α-*isopropylbenzyl*)-4-*phenyl*-1-*azabuta*-1,3-*diene*]*iron*(0) **9**.—Enneacarbonyldi-iron(0) (1.29 g, 3.54 mmol) and 1-(α-isopropylbenzyl)-4-phenyl-1-azabuta-1,3-diene **3** (0.93 g, 3.53 mmol) were allowed to react as described for complex **8**. Solvent removal followed by chromatography (SiO_2; light petroleum–diethyl ether, 15:1) gave a 3:1 mixture of **9a** and **9b** as an orange solid (0.65 g, 46%); ν_{max}(hexane)/cm^{-1} 2060vs, 1995vs and 1980vs (C≡O); δ_H(220 MHz) 0.73 and 0.75 (3 H, d, *J* 6, Me **9a**, **9b**), 0.9 and 0.92 (3 H, d, *J* 6, Me **9a**, **9b**), 1.9 (1 H, m, C*H*Me$_2$), 2.7 and 2.8 (1 H, d, *J* 6, C*H*Pr^i **9a**, **9b**), 3.1 and 3.15 (1 H, d, *J* 10, 4-H **9a**, **9b**), 5.45 and 5.55 (1 H, dd, *J* 3 and 10, 3-H **9b**, **9a**), 6.5 and 6.7 (1 H, d, *J* 3, 2-H **9b**, **9a**) and 7.15–7.4 (5 H, m, Ph); *m*/*z* (FAB): 404 (M$^+$ + 1, 97%), 376 (11, MH − CO), 347 (100, M − 2CO), 319 (97, M − 3CO) and 264 [44, MH − Fe(CO)$_3$].

Tricarbonyl[1-(α-t-*butylbenzyl*)-4-*phenyl*-1-*azabuta*-1,3-*diene*]*iron*(0) **10**.—Enneacarbonyldi-iron(0) (0.29 g, 0.80 mmol) and 1-(α-t-butylbenzyl)-4-phenyl-1-azabuta-1,3-diene **4** (0.19 g, 0.69 mmol) were allowed to react as described for complex **8**. Solvent removal followed by chromatography (SiO_2; light petroleum–diethyl ether, 15:1) gave a 93:7 mixture of **10a** and **10b** as a yellow solid (0.05 g, 17%); ν_{max}(hexane)/cm^{-1} 2060vs, 1995vs and 1980vs (C≡O); δ_H(400 MHz) 0.85 and 0.87 (9 H, s, Bu^t **10b**, **10a**), 2.70 and 2.90 (1 H, s, CHBu^t **10a**, **10b**), 3.08 and 3.10 (1 H, d, *J* 10, 4-H **10a**, **10b**), 5.38 and 5.47 (1 H, dd, *J* 3 and 10, 3-H **10b**, **10a**), 6.45 and 6.65 (1 H, d, *J* 3 Hz, 2-H **10b**, **10a**) and 7.15–7.49 (10 H, m, 2 × Ph); *m*/*z* (FAB): 418 (M$^+$ + 1, 100%), 390 (8, MH − CO), 361 (15, M − 2CO), 334 (82, MH − 3CO) and 278 [58, MH − Fe(CO)$_3$].

Tricarbonyl[1-(α-*ethylethyl*)-4-*phenyl*-1-*azabuta*-1,3-*diene*]*iron*(0) **17**.—Enneacarbonyldi-iron(0) (1.34 g, 3.68 mmol) and 1-(α-ethylethyl)-4-phenyl-1-azabuta-1,3-diene **13** (0.69 g, 3.69 mmol) were allowed to react as described for complex **8**. Solvent removal followed by chromatography (SiO_2; dichloromethane) gave a 1:1 mixture of **17a** and **17b** as an orange–brown solid (0.52 g, 43%); ν_{max}(hexane)/cm^{-1} 2050vs, 1990vs and 1975vs (C≡O); δ_H(220 MHz) 0.9 (3 H, t, *J* 7, CH$_2$CH_3), 1.15 (3 H, d, *J* 6, CHCH_3), 1.5 (2 H, m, CH_2CH$_3$), 1.85 [1 H, m, C*H*(Et)Me], 3.0 and 3.05 (1 H, d, *J* 10, 4-H), 5.5 and 5.55 (1 H, dd, *J* 3 and 10 Hz, 3-H), 6.55 and 6.6 (1 H, d, *J* 3 Hz, 2-H) and 7.2–7.55 (5 H, m, Ph); *m*/*z* (FAB): 328 (M$^+$ + 1, 100%), 300 (26, MH − CO), 272 (26, MH − 2CO), 244 (28, MH − 3CO) and 188 [24, MH − Fe(CO)$_3$].

Tricarbonyl[1-(1-*isopropylethyl*)-4-*phenyl*-1-*azabuta*-1,3-*diene*]*iron*(0) **18**.—Enneacarbonyldi-iron(0) (1.31 g, 3.60 mmol) and 1-(1-isopropylethyl)-4-phenyl-1-azabuta-1,3-diene **14** (0.73 g, 3.63 mmol) were allowed to react as described for complex **8**. Solvent removal followed by chromatography (SiO_2; dichloromethane) gave a 1:1 mixture of **18a** and **18b** as an orange solid (0.69 g, 56%); ν_{max}(hexane)/cm^{-1} 2050vs, 1995vs and 1975vs (C≡O); δ_H(220 MHz) 0.8–1.0 (9 H, m, 3 × Me), 1.6–1.7 [1 H, m, C*H*(CH$_3$)$_2$], 1.75–1.85 [1 H, m, C*H*(Me)Pr^i], 2.95 and 3.0 (1 H, d, *J* 9, 4-H), 5.45 and 5.5 (1 H, dd, *J* 3 and 9 Hz, 3-H), 6.55 and 6.65 (1 H, d, *J* 3, 2-H) and 7.15–7.3 (5 H, m, Ph); *m*/*z* (FAB): 342 (M$^+$ + 1, 100%), 314 (20, MH − CO), 286 (24, MH − 2CO), 258 (19, MH − 3CO) and 202 [78, MH − Fe(CO)$_3$].

Tricarbonyl[1-(α-t-*butylethyl*)-4-*phenyl*-1-*azabuta*-1,3-*diene*]*iron*(0) **19**.—Enneacarbonyldi-iron(0) (1.31 g, 3.60 mmol) and 1-(α-t-butylethyl)-4-phenyl-1-azabuta-1,3-diene **11** (0.77 g, 3.58 mmol) were allowed to react as described for complex **8**. Solvent removal followed by chromatography (SiO_2; light petroleum–diethyl ether, 15:1) gave a 94:6 mixture of **19a** and **19b** as an orange solid (0.35 g, 28%); ν_{max}(hexane)/cm^{-1} 2050vs, 1995vs and 1975vs (C≡O); δ_H(400 MHz): 0.85 and 0.89 (9 H, s, Bu^t **19a**, **19b**), 0.95 and 1.04 (3 H, d, *J* 6, CHCH_3 **19b**, **19a**), 1.63 and 2.19 [1 H, q, *J* 6, C*H*(Me)Bu^t **19a**, **19b**], 2.95 and 3.00 (1 H, d, *J* 9, 4-H **19b**, **19a**), 5.36 and 5.41 (1 H, dd, *J* 4 and 9, 3-H **19a**, **19b**), 6.50 and 6.81 (1 H, d, *J* 4, 2-H **19a**, **19b**) and 7.10–7.25 (5 H, m, Ph); *m*/*z* (FAB): 356 (M$^+$ + 1, 100%), 328 (16, MH − CO), 300 (26, MH − 2CO), 271 (33, M − 3CO) and 216 [70, MH − Fe(CO)$_3$].

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