

Nucleophilic Addition to Tricarbonyliron(0) Complexes of 1-Aza-1,3-dienes and the Production of Pyrroles

Timothy N. Danks and Susan E. Thomas*

Department of Chemistry, University of Warwick, Coventry CV4 7AL

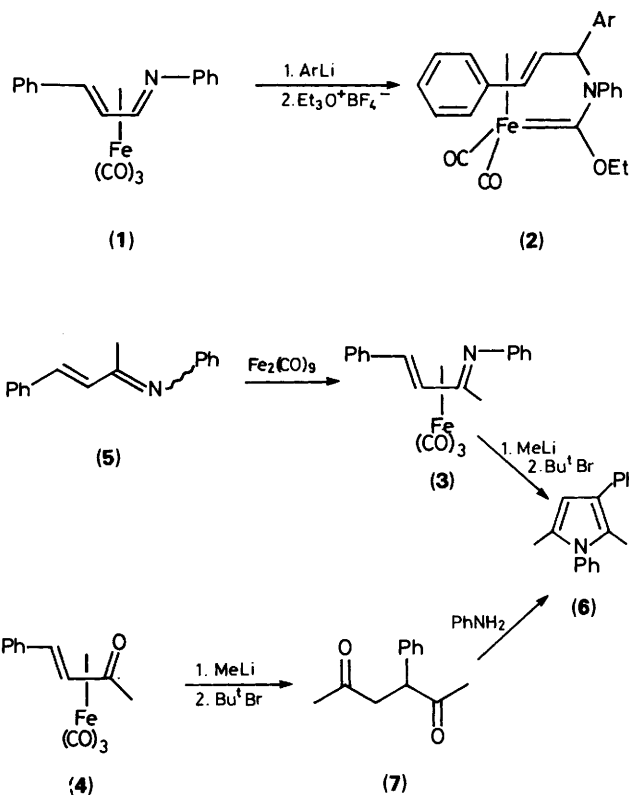
The synthesis of a number of novel tricarbonyl(1-aza-1,3-diene)iron(0) complexes and their reactions with methyl-lithium are described. Addition proceeds under mild conditions and, in general, occurs at a metal carbonyl ligand; this leads *via* an unprecedented reaction to the production of several novel pyrroles.

Tricarbonyliron(0) complexes of 1-aza-1,3-dienes were first reported in 1967.¹ Whilst carbonyl-phosphine exchange has been studied in detail,² the reactivity of the organic ligand of these complexes has received very little attention. Protonation has been shown to occur on the nitrogen atom of tricarbonyl(1,4-diphenyl-1-azabuta-1,3-diene)iron(0) (1),³ and recently, it was discovered that treatment of (1) with aryl-lithium reagents followed by alkylation with $\text{Et}_3\text{O}^+\text{BF}_4^-$ affords novel η^4 -styrene complexes (2).⁴

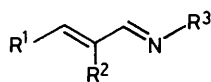
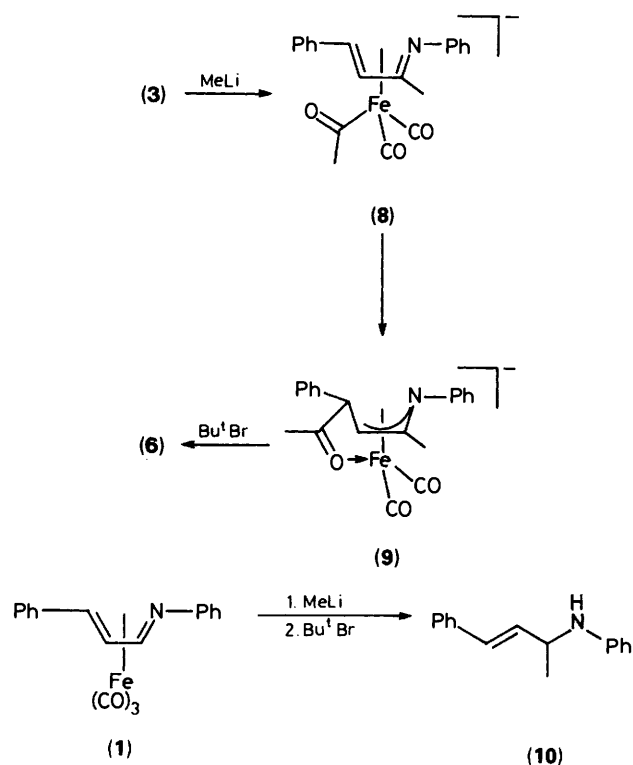
Our interest in the reactivity of transition metal ligands containing heteroatoms led us to investigate nucleophilic attack on tricarbonyliron(0) complexes of α,β -unsaturated ketones. Addition of a range of hard nucleophiles to tricarbonyliron(0) complexes of benzylideneacetone and analogues resulted in the clean production of 1,4-diketones.^{5,6} In order to investigate the effect on reactivity of replacing the oxygen atom in the ligand with a substituted nitrogen atom, we synthesised the tricarbonyliron(0) complex of 1,4-diphenyl-2-methyl-1-azabut-1,3-diene, (3), which may be regarded as a nitrogen-containing analogue of tricarbonyl(benzylideneacetone)iron(0), (4). The results of nucleophilic attack on complex (3) and other tricarbonyl(1-aza-1,3-diene)iron(0) complexes are described in detail below. Part of this work has been the subject of a preliminary publication.⁷

Results and Discussion

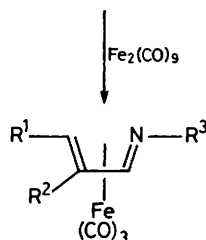
The novel complex tricarbonyl(2-methyl-1,4-diphenyl-1-azabuta-1,3-diene)iron(0) (3) was synthesised as follows. Condensation of aniline with benzylideneacetone under zinc chloride catalysis⁸ produced a mixture of the stereoisomeric 1-azabuta-1,3-dienes (5). Separation of the two isomers proved unnecessary as complexation to the tricarbonyliron(0) moiety occurred selectively. Heating the mixture of the two isomers with $[\text{Fe}_2(\text{CO})_9]$ at 40 °C for 3 h followed by filtration and concentration of the reaction mixture gave a dark red oil which on crystallisation produced red crystals of a single compound which were identified as the air-stable complex (3) (40%) on the basis of spectroscopic and analytical data. The stereochemistry about the carbon-nitrogen bond in (3) was predicted to be *E* as strong steric interactions between an *ortho*-proton of the *N*-phenyl group and the C-4 proton would make the Z_{CN} stereoisomer of (3) relatively unstable. This prediction was confirmed by NOE difference spectroscopy; irradiation of the methyl protons of (3) enhanced the signal due to the *ortho*-protons of the *N*-phenyl group (9%) and the signal due to the C-3 proton (7%). There was no evidence for the formation of the Z_{CN} isomer of (3). The outcome of nucleophilic attack on (3) was then investigated using methyl-lithium as a representative hard carbon nucleophile. Complex (3) was stirred with methyl-



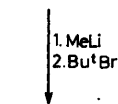
lithium at -78 °C for 6.5 h and the reaction mixture quenched with a proton source. Chromatography led to the isolation of a straw-coloured liquid as the major reaction product which gave spectroscopic data consistent with the structure of the novel pyrrole (6) (70%). The identity of the major product of the reaction was confirmed by an independent synthesis of the pyrrole (6). The 1,4-diketone (7), prepared by the action of methyl-lithium on tricarbonyl(benzylideneacetone)iron(0) (4),^{5,6} when heated with aniline at 150 °C for 5.5 h gave a straw-coloured liquid which was spectroscopically identical with (6) (65%). Thus, it appears that methyl-lithium attacks complex (3) at a metal-carbonyl ligand to give a metal-acyl anion, (8). It is envisaged that subsequent transfer of the acyl group to C-4 of the 1-aza-1,3-diene ligand to give an intermediate (9) is followed by condensation of the 1-aza-allyl group and the ketone to give rise to the product pyrrole (6). The low temperature at which the conversion of complex (3) into the pyrrole (6) occurs contrasts strongly with the temperature necessary to convert the diketone (7) into the pyrrole (6)—attempts to convert the diketone (7) into the pyrrole (6) at temperatures lower than 150 °C failed to



- (11) R¹ = Ph, R² = H, R³ = CH₂Ph
 (14) R¹ = Ph, R² = H, R³ = CHMePh
 (17) R¹ = Me, R² = H, R³ = CHMePh
 (20) R¹ = Ph, R² = Me, R³ = CHMePh



- (12) R¹ = Ph, R² = H, R³ = CH₂Ph
 (15) R¹ = Ph, R² = H, R³ = CHMePh
 (18) R¹ = Me, R² = H, R³ = CHMePh



- (13) R¹ = Ph, R² = H, R³ = CH₂Ph
 (16) R¹ = Ph, R² = H, R³ = CHMePh
 (19) R¹ = Me, R² = H, R³ = CHMePh

produce any evidence for the formation of the pyrrole (6) (as detected by 220 MHz ¹H NMR spectroscopy) within 6.5 h—and

suggests that the metal moiety not only acts as a carbonylating agent but is also involved in the ring-closure step of pyrrole formation.⁹

In order to examine further this novel approach to the pyrrole ring, a range of 1-aza-1,3-dienes bearing different substituents were prepared, complexed to the tricarbonyliron(0) unit, and treated with methyl-lithium.

Initially, the readily available air-stable complex tricarbonyl-(1,4-diphenyl-1-azabuta-1,3-diene)iron(0) (1)¹ was examined. Complex (1) was stirred with methyl-lithium at -78 °C for 6.5 h and the reaction mixture quenched with an excess of t-butyl bromide. Chromatography led to the isolation of the major product as white crystals which were identified as the amine (10) (69%). Nucleophilic attack on complex (1) thus occurred at C-2 of the ligand. Since the amine (10) is also the major product (85%) of the reaction between 1,4-diphenyl-1-azabuta-1,3-diene and methyl-lithium, it is conceivable that a preliminary dissociation step has occurred in this reaction. Isolation of η⁴-styrene complexes (2), upon treatment of compound (1) with aryl-lithium reagents and Et₃O⁺BF₄⁻, however, suggests that preliminary dissociation is probably not the major pathway of the reaction.

The reactions between methyl-lithium and 1-aza-1,3-diene complexes bearing substituents other than phenyl on the nitrogen atom were examined.

Condensation of benzylamine with cinnamaldehyde gave the 1-aza-1,3-diene (11) as pale yellow crystals (80%). Compound (11) when stirred with [Fe₂(CO)₉] at 45 °C for 2 h followed by filtration and concentration of the mixture produced a deep red gum which was identified as the novel tricarbonyliron(0) complex (12). Although complex (12) was stable as a gum if maintained under a nitrogen atmosphere, attempts to crystallise (12) were frustrated by its instability in solution. The crude product was, therefore, treated with methyl-lithium without further purification. Complex (12) was stirred with methyl-lithium at -23 °C for 2 h and the reaction mixture quenched with t-butyl bromide. Chromatography of the product mixture led to the isolation of pale yellow crystals of the novel pyrrole (13) [50% based on 1-aza-1,3-diene (11)].

The tricarbonyliron(0) complex of the 1-aza-1,3-diene derived from cinnamaldehyde and 1-phenylethylamine proved to be air-stable. Condensation of cinnamaldehyde with 1-phenylethylamine gave 4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene (14) as pale yellow crystals (90%). Compound (14) when heated with [Fe₂(CO)₉] followed by filtration and concentration of the mixture, and chromatography of the residue led to the isolation of red crystals which were identified as a 1:1 mixture of the two diastereoisomeric forms of the novel air-stable complex (15) (52%). Recrystallisation of complex (15) gave a sample slightly enriched in one diastereoisomer (4:3) and examination of this sample of complex (15) by NOE difference spectroscopy revealed conformational information about the two diastereoisomers. In the 'major' diastereoisomer, (15a), irradiation of 2-H enhanced the signals due to 3-H (7%), the methine proton of the 1-phenylethyl group (9%), and also the signal of the methyl protons of the 1-phenylethyl group (3%). Irradiation of the methyl protons of the 1-phenylethyl group enhanced the signals due to the methine proton of the 1-phenylethyl group (10%) and also the signal due to 2-H (7%). In the 'minor' diastereoisomer, (15b), however, irradiation of 2-H enhanced the signals due to 3-H (8%) and the methine proton of the 1-phenylethyl group (8%) but not the signal due to the methyl protons of the 1-phenylethyl group. Irradiation of the methyl protons of the 1-phenylethyl group enhanced the signal of the methine proton of the 1-phenylethyl group (12%) but not the signal of 2-H. These results correspond well with predictions made using the molecular modelling program CHEM-X for the

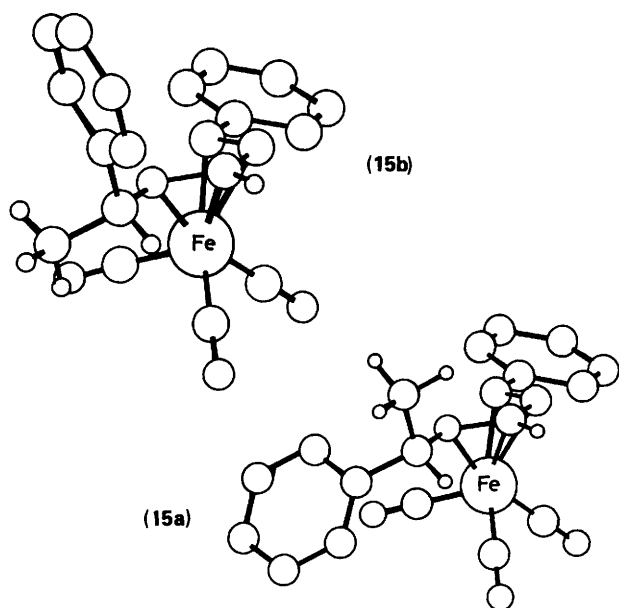


Figure. Diastereoisomers of complex (15) in their most stable conformation as predicted by CHEM-X.

most stable conformation of each diastereoisomer (see Figure). Reaction of complex (15) [(15a):(15b), 1:1] with methyl-lithium at -40°C for 4 h followed by the standard work-up procedure resulted in the isolation of the novel pyrrole (16) as an orange liquid (50%).

Experiments were performed to discover the effect on reactivity of replacing the phenyl group at C-4 with an alkyl group. Crotonaldehyde was condensed with 1-phenylethylamine to give the 1-aza-1,3-diene (17) as a pale yellow liquid (90%). Compound (17) when treated with $[\text{Fe}_2(\text{CO})_9]$ gave a 1:1 diastereoisomeric mixture of the tricarbonyliron(0) complex (18) which proved to be very air-sensitive and was thus treated directly with methyl-lithium; standard work-up led to the isolation of white crystals of the novel pyrrole (19) in 25% yield [based on (17)]. The low yield of pyrrole obtained from this reaction almost certainly reflects the instability of complex (18).

Finally, repeated attempts to generate a tricarbonyliron(0) derivative of 1-aza-1,3-diene (20), formed from α -methylcinnamaldehyde and 1-phenylethylamine, proved to be unsuccessful and thus prevented determination of the effect on reactivity of introducing an alkyl group at C-3 of the 1-aza-1,3-diene ligand.

Experimental

Reactions under nitrogen were performed using standard vacuum line and Schlenk tube techniques.¹⁰ Diethyl ether was dried over sodium wire and light petroleum refers to the fraction boiling in the range $30\text{--}40^{\circ}\text{C}$. Enneacarbonyliron(0),¹¹ 2-methyl-1,4-diphenyl-1-azabuta-1,3-diene (5),⁸ 3-phenylhexane-2,5-dione (7),⁶ and tricarbonyl(1,4-diphenyl-1-azabuta-1,3-diene)iron(0) (1)¹ were prepared according to published procedures whilst methyl-lithium (1.4M in diethyl ether) was used as supplied by Aldrich. Chromatography was performed on SiO_2 (Merck, $40\text{--}63\ \mu\text{m}$). M.p.s were obtained on a Gallenkamp capillary m.p. apparatus and are uncorrected. Elemental analyses were performed by Butterworth Laboratories Ltd. and City 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 (unless stated otherwise) on Perkin-Elmer R34 (220 MHz ^1H) and Bruker WH 400 (400MHz ^1H , 100.6 MHz ^{13}C) spectrometers. Mass spectra were recorded on a Kratos MS 80 instrument using EI and FAB (matrix—*m*-nitrobenzyl alcohol¹²) techniques. Calculations using CHEM-X (a molecular modelling program developed and designed by Chemical Design Ltd., Oxford) were performed on structures generated from the X-ray crystal structure data¹³ of tricarbonyl(1,4-diphenyl-1-azabuta-1,3-diene)iron(0) (1) using the default parameters of the program which only take into account van der Waals interactions.

Preparation of Tricarbonyl(2-methyl-1,4-diphenyl-1-azabuta-1,3-diene)iron(0) (3).—Enneacarbonyliron(0) (1.30 g, 3.57 mmol) and 2-methyl-1,4-diphenyl-1-azabuta-1,3-diene (5) (0.79 g, 3.57 mmol) were added to toluene (25 ml) and the resulting mixture maintained at 40°C under nitrogen for 3 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 crystallised from heptane. A solution of the product in diethyl ether was filtered through a plug of alumina and the solvent removed from the filtrate under reduced pressure to yield fine orange-red crystals of complex (3) (0.51 g, 40%), m.p. $129\text{--}130^{\circ}\text{C}$ (Found: C, 63.0; H, 4.15; N, 3.8. $\text{C}_{19}\text{H}_{15}\text{FeNO}_3$ requires C, 63.18; H, 4.18; N, 3.87%); ν_{max} (hexane) 2060vs, 1995vs, and 1983vs cm^{-1} ($\text{C}\equiv\text{O}$); δ_{H} (220 MHz) 2.42 (3 H, s, CH_3), 3.20 (1 H, d, J 10 Hz, 4-H), 5.60 (1 H, d, J 10 Hz, 3-H), and 6.70–7.50 (10 H, m, $2 \times \text{Ph}$); δ_{C} 16.5 (CH_3), 59.7 (C-4), 71.3 (C-3), 124.1 (C-2), 121.4, 123.0, 126.5, 126.6, 128.5, 128.6, 139.3, and 149.8 ($2 \times \text{Ph}$); m/z (FAB) 362 ($M^+ + 1$, 14%), 333 (48, $M - \text{CO}$), 305 (50, $M - 2\text{CO}$), and 277 (100, $M - 3\text{CO}$).

Reaction of Methyl-lithium with Tricarbonyl(2-methyl-1,4-diphenyl-1-azabuta-1,3-diene)iron(0) (3).—Methyl-lithium (0.71 ml, 1.0 mmol) was added to a solution of tricarbonyl(2-methyl-1,4-diphenyl-1-azabuta-1,3-diene)iron(0) (3) (180 mg, 0.5 mmol) in diethyl ether (10 ml) at -78°C . The solution was stirred at -78°C for 6.5 h under an atmosphere of nitrogen and the resulting orange-brown solution was quenched with *t*-butyl bromide (1.37 g, 10.0 mmol) and allowed to warm to room temperature over 0.5 h. The dark brown mixture was filtered through a plug of alumina and the solvent removed under reduced pressure to yield an orange-brown oil which was chromatographed (SiO_2 ; light petroleum–diethyl ether, 4:1) to yield a straw coloured liquid which was identified as 2,5-dimethyl-1,3-diphenylpyrrole (6) (86 mg, 70%) by comparison of its ^1H NMR, IR and MS data with those of an authentic sample.

Reaction of 3-Phenylhexane-2,5-dione (7) with Aniline.—3-Phenylhexane-2,5-dione (7) (50 mg, 0.26 mmol) was added to aniline (24 mg, 0.26 mmol) and the mixture heated at 150°C for 5.5 h to yield a dark brown oil. The oil was chromatographed (SiO_2 ; light petroleum–diethyl ether, 4:1) to yield 2,5-dimethyl-1,3-diphenylpyrrole (6) as a straw coloured liquid (42 mg, 65%), b.p. $232\text{--}235^{\circ}\text{C}$ at 763 mmHg (Found: m/z 247.1352. $\text{C}_{18}\text{H}_{17}\text{N}$ requires 247.1361); δ_{H} (220 MHz) 2.08 (3 H, s, CH_3), 2.16 (3 H, s, CH_3), 6.16 (1 H, s, 4-H), and 7.20–7.50 (10 H, m, $2 \times \text{Ph}$); δ_{C} 12.1, 12.7 ($2 \times \text{CH}_3$), 106.5 (C-4), 121.0 (C-3), 125.0 (C-2), 128.5 (C-5), 124.9, 127.6, 127.7, 128.1, 128.3, 129.0, 137.3, and 138.8 ($2 \times \text{Ph}$); m/z (EI) 247 (M^+ , 100%).

Reaction of Methyl-lithium with Tricarbonyl(1,4-diphenyl-1-azabuta-1,3-diene)iron(0) (1).—Methyl-lithium (0.74 ml, 1.00 mmol) was added to a solution of (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) (1) (180 mg, 0.52 mmol) in diethyl ether (15 ml) at -78°C and the resulting orange solution stirred at -78°C for 6.5 h under an atmosphere of nitrogen.

The reaction was quenched with *t*-butyl bromide (0.685 g, 5.0 mmol) and allowed to warm to room temperature over 0.5 h. The resulting dark-brown mixture was filtered through a plug of alumina to remove the iron residues and the solvent removed under reduced pressure to yield a dark brown oil. The oil was chromatographed (SiO₂; light petroleum–diethyl ether, 9:1) to yield a white crystalline solid which was identified as the amine (10) (81 mg, 69%) by comparison of its ¹H NMR, IR, and MS data with those of an authentic sample.

Reaction of Methyl-lithium with 1,4-Diphenyl-1-azabuta-1,3-diene.—Methyl-lithium (2.14 ml, 3.0 mmol) was added to a solution of 1,4-diphenyl-1-azabuta-1,3-diene (300 mg, 1.45 mmol) in diethyl ether (30 ml) at –78 °C and the resulting solution stirred at –78 °C for 6.5 h under a nitrogen atmosphere. The reaction was quenched with *t*-butyl bromide (2.0 g, 14.5 mmol) and allowed to warm to room temperature over 0.5 h. The reaction mixture was filtered through a plug of alumina and the solvent removed under reduced pressure to yield a yellow oil. The oil was chromatographed (SiO₂; diethyl ether–light petroleum, 9:1) to yield the amine (10) as white crystals (275 mg, 85%), m.p. 49–50 °C (Found: C, 85.8; H, 7.8; N, 6.05. C₁₆H₁₇N requires C, 86.05; H, 7.68; N 6.27%); ν_{\max} (hexane) 3 420w (NH) and 1 605m cm⁻¹ (C=C); δ_{H} (220 MHz) 1.38 (3 H, d, *J* Hz, CH₃), 3.68 (1 H, br s, NH), 4.15 (1 H, m, CHCH₃), 6.23 (1 H, dd, *J* 7 and 11 Hz, CH=CHPh), and 6.50–7.50 (11 H, m, CH=CHPh and 2 × Ph); δ_{C} 21.9 (CH₃), 50.7 (CHCH₃), 113.3, 117.2, 126.2, 127.2, 128.4, 129.0, 129.1, 133.1, 136.8, and 147.3 (2 × Ph and PhCH=CH); *m/z* (EI) 223 (*M*⁺, 30%), 208 (18, *M* – CH₃), and 131 (100, *M* – NHPh).

Preparation of 1-Benzyl-4-phenyl-1-azabuta-1,3-diene (11).—Benzylamine (1.07 g, 10 mmol) was added to cinnamaldehyde (1.32 g, 10 mmol) at 0 °C and the resulting mixture stirred for 15 min. The yellow oil produced was dissolved in diethyl ether (20 ml) and dried (MgSO₄). Filtration and removal of solvent under reduced pressure yielded a yellow oil which crystallised when set aside at –20 °C for 12 h. Recrystallisation from diethyl ether at –78 °C yielded pale yellow crystals of the *title compound* (11) as pale yellow crystals (1.768 g, 80%), m.p. 27–28 °C (Found: C, 86.8; H, 6.95; N, 6.6. C₁₆H₁₅N requires C, 86.83; H, 6.84; N, 6.33%); ν_{\max} (hexane) 1 635s (C=N) and 1 620w cm⁻¹ (C=C); δ_{H} (220 MHz) 4.70 (2 H, s, CH₂), 6.90–7.60 (12 H, m, 3-H, 4-H, and 2 × Ph), and 8.17 (1 H, m, 2-H); δ_{C} 65.1 (CH₂), 126.8, 127.0, 127.9, 128.0, 128.4, 128.6, 129.0, 135.5, 139.0, (2 × Ph, and C-3), 141.8 (C-4), and 163.2 (C-2); *m/z* (EI) 221 (*M*⁺, 41%) and 91 (100, C₇H₇).

Preparation of 1-Benzyl-2-methyl-3-phenylpyrrole (13).—Enneacarbonyliron(0) (1.30 g, 3.57 mmol) and 1-benzyl-4-phenyl-1-azabuta-1,3-diene (11) (0.79 g, 3.57 mmol) were added to toluene (20 ml) and heated at 45 °C for 2 h under an atmosphere of nitrogen to yield a deep red mixture. The mixture was filtered through a plug of alumina to remove the iron residues and the solvent removed under reduced pressure to give a deep red gum. The gum was identified as tricarbonyl(1-benzyl-4-phenyl-1-azabuta-1,3-diene)iron(0) (12) on the basis of its ¹H NMR spectrum δ_{H} (220 MHz) 3.09 (1 H, d, *J* 10 Hz, 4-H), 3.47 (1 H, d, *J* 15 Hz, 1 H of PhCH₂N=), 3.87 (1 H, d, *J* 15 Hz, 1 H of PhCH₂N=), 5.55 (1 H, dd, *J* 3 and 10 Hz, 3-H), 6.70 (1 H, d, *J* 3 Hz, 2-H), and 7.00–7.50 (10 H, m, 2 × Ph). Because of its air-sensitivity in solution the crude product was used in the second stage of the reaction without further purification. Methyl-lithium (5.1 ml, 7.14 mmol) was added to a solution of crude (12) in diethyl ether (30 ml) at –23 °C and the resulting solution stirred at –23 °C for 2 h under an atmosphere of nitrogen to yield a brown mixture. After quenching with *t*-butyl bromide (9.78 g, 71.4 mmol), the mixture was filtered through a

plug of alumina and the solvent removed under reduced pressure to leave a brown gum. The gum was chromatographed (SiO₂; light petroleum–diethyl ether, 4:1) to yield 1-benzyl-2-methyl-3-phenylpyrrole (13) as pale yellow crystals (0.44 g, 50%), m.p. 53.5–54.5 °C (Found: *m/z* 247.1356. C₁₈H₁₇N requires 247.1361); δ_{H} (220 MHz) 2.37 (3 H, s, CH₃), 5.11 (2 H, s, CH₂), 6.37 (1 H, d, *J* 3 Hz, 4-H), 6.73 (1 H, d, *J* 3 Hz, 5-H), and 7.00–7.60 (10 H, m, 2 × Ph); δ_{C} 10.7 (CH₃), 50.6 (CH₂), 107.6 (C-4), 120.4 (C-5), 122.5 (C-3), 125.1 (C-2), 125.0, 126.3, 127.3, 127.8, 128.2, 128.6, 137.4, and 138.0 (2 × Ph); *m/z* (EI) 247 (*M*⁺, 49%), and 91 (100, C₇H₇).

Preparation of 4-Phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene (14).—1-Phenylethylamine (2.42 g, 20 mmol) was added to cinnamaldehyde (2.64 g, 20 mmol) at 0 °C and the resulting mixture stirred at 0 °C for 5 min to yield a yellow solid. The solid was dissolved in diethyl ether and the resulting solution dried over MgSO₄. After filtration, solvent was removed under reduced pressure and the resulting yellow oil crystallised from diethyl ether and then dried *in vacuo* for 24 h to yield the *title compound* (14) as pale yellow crystals (4.23 g, 90%), m.p. 40–41 °C (Found: C, 86.95; H, 7.4; N, 6.1. C₁₇H₁₇N requires C, 86.76; H, 7.28; N, 5.95%); ν_{\max} (Nujol) 1 640s (C=N) and 1 620m cm⁻¹ (C=C); δ_{H} (220 MHz) 1.57 (3 H, d, *J* 7 Hz, CH₃), 4.43 (1 H, q, *J* 7 Hz, CHCH₃Ph), 6.80–7.60 (12 H, m, 2 × Ph, 3-H and 4-H), and 8.12 (1 H, d, *J* 9 Hz, 2-H); δ_{C} 24.4 (CHCH₃Ph), 69.6 (CHCH₃Ph), 126.5, 126.8, 127.1, 128.2, 128.4, 128.7, 128.9, 135.6, 144.7, (2 × Ph and C-3) 141.6 (C-4), and 161.2 (C-2); *m/z* (EI) 235 (*M*⁺, 40%), 220 (33, *M* – CH₃), and 105 (100, CHCH₃Ph).

Preparation of Tricarbonyl[4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene]iron(0) (15).—Enneacarbonyliron(0) (1.30 g, 3.57 mmol) and 4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene (14) (0.839 g, 3.57 mmol) were added to toluene (20 ml) and the mixture was stirred at 50 °C for 2 h under an atmosphere of nitrogen to yield a deep red mixture. This mixture was filtered and the solvent removed under reduced pressure to give a dark red oil which was chromatographed (SiO₂; light petroleum–ethyl acetate, 20:1) to yield orange crystals of a 1:1 mixture of the two diastereoisomeric forms of the *title compound* (15) (0.70 g, 52%) (Found: C, 64.2; H, 4.6; N, 3.8. C₂₀H₁₅FeNO₃ requires C, 64.02; H, 4.57; N, 3.73%); ν_{\max} (hexane) 2 080vs, 2 017vs, and 1 985vs cm⁻¹ (C=O); δ_{H} [diastereoisomer (15a)] (400 MHz; C₆D₆–CDCl₃, 1:1) 1.31 (3 H, d, *J* 6 Hz, CHCH₃Ph), 2.94 (1 H, q, *J* 6 Hz, CHCH₃Ph), 3.04 (1 H, d, *J* 9 Hz, 4-H), 5.26 (1 H, dd, *J* 3 and 9 Hz, 3-H) 6.39 (1 H, d, *J* 3 Hz, 2-H), and 7.0–7.3 (10 H, m, 2 × Ph); δ_{H} [diastereoisomer (15b)] (400 MHz; C₆D₆–CDCl₃, 1:1) 1.40 (3 H, d, *J* 6 Hz, CHCH₃Ph), 2.96 (1 H, q, *J* 6 Hz, CHCH₃Ph), 3.10 (1 H, d, *J* 9 Hz, 4-H), 5.16 (1 H, dd, *J* 3 and 9 Hz, 3-H), 6.24 (1 H, d, *J* 3 Hz, 2-H), and 7.0–7.3 (10 H, m, 2 × Ph); δ_{C} [diastereoisomer (15a)] (C₆D₆–CDCl₃, 1:1) 29.1 (CHCH₃Ph), 61.0 (CHCH₃Ph), 68.8 (C-4), 72.7 (C-3), and 110.7 (C-2) (Ph region not assigned); δ_{C} [diastereoisomer (15b)] (C₆D₆–CDCl₃, 1:1) 27.1 (CHCH₃Ph), 62.2 (CHCH₃Ph), 68.1 (C-4), 72.4 (C-3), and 111.6 (C-2) (Ph region not assigned); *m/z* (FAB) 376 (*M*⁺ + 1, 78%), 347 (10, *M* – CO), 319 (51, *M* – 2CO), and 291 (73, *M* – 3CO).

Preparation of 2-Methyl-3-phenyl-1-(1-phenylethyl)pyrrole (16).—Methyl-lithium (1.96 ml, 2.74 mmol) was added to a solution of tricarbonyl[4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene]iron(0) (15) (315 mg, 1.37 mmol) in diethyl ether (20 ml) and the resulting solution stirred at –40 °C for 4 h under an atmosphere of nitrogen to yield a dark orange mixture. The reaction was quenched with *t*-butyl bromide (3.75 g, 27.4 mmol) and allowed to warm to room temperature over 0.5 h. The mixture was filtered through a plug of alumina to remove the iron residues and the solvent removed under reduced pressure

to yield a dark oil. The oil was chromatographed (SiO_2 ; light petroleum–diethyl ether, 4:1) to yield the title compound (**16**) as an orange liquid (179 mg, 50%) b.p. 195–200 °C at 763 mmHg (Found: m/z 261.1513. $\text{C}_{19}\text{H}_{19}\text{N}$ requires 261.1517); δ_{H} (220 MHz) 1.86 [3 H, d, J 9 Hz, $\text{CH}(\text{CH}_3)\text{Ph}$], 2.23 (3 H, s, CCH_3), 5.40 [1 H, q, J 9 Hz, $\text{CH}(\text{CH}_3)\text{Ph}$], 6.43 (1 H, d, J 4 Hz, 4-H), 6.95 (1 H, d, J 4 Hz, 5-H), and 7.00–7.60 (10 H, m, 2 \times Ph); δ_{C} 10.8 (C- CH_3), 22.3 [$\text{CH}(\text{CH}_3)\text{Ph}$], 55.1 [$\text{CH}(\text{CH}_3)\text{Ph}$], 107.4 (C-4), 116.6 (C-5), 122.4 (C-3), 125.2 (C-2), 124.9, 125.6, 127.0, 128.0, 128.1, 128.6, 137.4, and 143.5 (2 \times Ph); m/z (EI) 261 (M^+ , 15%), 157 (25, $M + 1 - \text{CHCH}_3\text{Ph}$), and 105 (100, CHCH_3Ph).

Preparation of 4-Methyl-1-(1-phenylethyl)-1-azabuta-1,3-diene (17).—1-Phenylethylamine (2.42 g, 20 mmol) was added to crotonaldehyde (1.40 g, 20 mmol) at 0 °C and stirred for 0.25 h to yield a yellow oil. The oil was dissolved in diethyl ether (10 ml) and the resulting solution dried (MgSO_4). After filtration the solvent was removed under reduced pressure to yield a yellow oil which was dried *in vacuo* for 24 h to give the title compound (**17**) as a pale yellow liquid (3.11 g, 90%), b.p. 220–225 °C at 14 mmHg (decomp.) (Found: m/z 173.1202. $\text{C}_{12}\text{H}_{15}\text{N}$ requires 173.1204); ν_{max} (thin film) 1 660s (C=N) and 1 627m cm^{-1} (C=C); δ_{H} (220 MHz) 1.53 (3 H, d, J 9 Hz, CHCH_3Ph), 1.87 (3 H, d, J 6 Hz $\text{CH}_3\text{C}=\text{CH}$), 4.36 (1 H, q, J 6 Hz, CHCH_3Ph), 6.10–6.50 (2 H, m, 3-H and 4-H), 7.20–7.60 (5 H, m, Ph), and 8.00 (1 H, d, J 10 Hz, 2-H); δ_{C} 18.0 (4- CH_3), 24.3, (CHCH_3Ph), 69.2 (CHCH_3Ph), 126.3, 126.5, 128.1, 144.8 (Ph), 131.9 (C-3), 140.2 (C-4), and 161.0 (C-2); m/z (EI) 173 (M^+ , 23%), 158 (30, $M - \text{CH}_3$), and 105 (100, CHCH_3Ph).

Preparation of 2,3-Dimethyl-1-(1-phenylethyl)pyrrole (19).—Enneacarbonyl-di-iron (1.30 g, 3.57 mmol) and 4-methyl-1-(1-phenylethyl)-1-azabuta-1,3-diene (**17**) (0.62 g, 3.57 mmol) were added to toluene (20 ml) and heated at 50 °C for 2 h under an atmosphere of nitrogen to yield a dark brown mixture. The mixture was filtered to remove the iron residues and the solvent removed under reduced pressure to give a dark oil identified as a 1:1 diastereoisomeric mixture of the unstable complex tricarbonyl[4-methyl-1-(1-phenylethyl)-1-azabuta-1,3-diene]iron(0) (**18**) by its ^1H NMR spectrum: δ_{H} (220 MHz) 1.20–1.50 (12 H, m, 4 \times CH_3), 1.53 (1 H, m, 4-H), 1.88 (1 H, m, 4-H), 2.95 [2 H, m, $\text{CH}(\text{CH}_3)\text{Ph}$], 4.83 (1 H, dd, J 3 and 10 Hz, 3-H), 4.93 (1 H, dd, J 3 and 10 Hz, 3-H), 6.33 (1 H, d, J 3 Hz, 2-H), 6.55 (1 H, d, J 3 Hz, 2-H), and 7.10–7.60 (10 H, m, 2 \times Ph). The crude oil was dissolved in diethyl ether (20 ml), cooled to –23 °C and methyl-lithium (5.1 ml, 7.14 mmol) was added to the solution which was stirred at –23 °C for 2 h. After quenching with *t*-butyl bromide (9.78 g, 71.4 mmol) the resulting dark brown mixture was filtered through a plug of alumina to remove the iron residues and the solvent removed under reduced pressure to yield a dark brown oil which was chromatographed (SiO_2 ; light petroleum–diethyl ether, 7:2) to give 2,3-dimethyl-1-(1-phenylethyl)pyrrole (**19**) as white crystals (0.18 g, 25%), m.p. 68–69 °C (Found: m/z 199.1362. $\text{C}_{14}\text{H}_{17}\text{N}$ requires 199.1361); δ_{H} (220 MHz) 1.79 (3 H, d, J 8 Hz, CHCH_3Ph), 1.99 (3 H, s, CCH_3), 2.04 (3 H, s, CCH_3), 5.26 (1 H, q, J 8 Hz, CHCH_3Ph), 6.08 (1 H, d, J 3 Hz, H-4), 6.88 (1 H, d, J 3 Hz, 5-H), and 7.20–7.50 (5 H, m, Ph); δ_{C} 9.6, 11.2 (2 \times CCH_3),

22.3 (CHCH_3Ph), 54.9 (CHCH_3Ph), 108.2 (C-4), 114.9 (C-3), 115.4 (C-5) 124.5 (C-2), 125.6, 126.9, 128.5, and 143.9 (Ph); m/z (EI) 199 (M^+ , 58%), 105 (100, CHCH_3Ph), and 95 ($M + 1 - \text{CHCH}_3\text{Ph}$).

Preparation of 3-Methyl-4-phenyl-1-(1-phenylethyl)-1-azabuta-1,3-diene (20).—1-Phenylethylamine (2.42 g, 20 mmol) was added to α -methylcinnamaldehyde (2.92 g, 20 mmol) and the resultant mixture stirred at 0 °C for 10 min to yield a yellow oil. The oil was dissolved in diethyl ether and the resulting solution dried (MgSO_4). After filtration, the solvent was removed under reduced pressure to yield a yellow oil which crystallised with time. The crystals were recrystallised from diethyl ether to yield the title compound (**20**) as pale yellow crystals (3.98 g, 80%), m.p. 45–46 °C (Found: C, 86.45; H, 7.8; N, 5.45. $\text{C}_{18}\text{H}_{19}\text{N}$ requires C, 86.70; H, 7.68; N, 5.62%); ν_{max} (Nujol) 1 630 br s (C=N) and cm^{-1} (C=C); δ_{H} (220 MHz) 1.57 (3 H, d, J 5 Hz, CHCH_3Ph), 2.23 (3 H, s, $\text{CH}=\text{CCH}_3$), 4.53 (1 H, q, J 5 Hz, CHCH_3Ph), 6.87 (1 H, s, 4-H), 7.20–7.70 (10 H, m, 2 \times Ph), and 8.18 (1 H, s, 2-H); δ_{C} 13.1 (3- CH_3), 24.9 (CHCH_3Ph), 69.0 (CHCH_3Ph), 126.3, 126.4, 127.2, 127.9, 128.0, 128.9, 136.4, 145.3 (2 \times Ph), 136.9 (C-3), 138.3 (C-4), and 163.7 (C-2); m/z (EI) 249 (M^+ , 69%), 234 (18, $M - \text{CH}_3$), 144 (69, $M - \text{PhCHCH}_3$), and 105 (100, PhCHCH_3).

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