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

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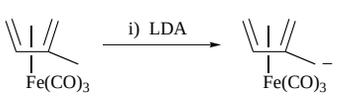
Treatment of (2-methyl-1-azabuta-1,3-diene)tricarbonyliron(0) complexes with lithium diethylamide followed by a proton source leads to the formation of (enamine)tricarbonyliron(0) complexes in good yield.

Introduction

In recent years the reactions of tricarbonyliron(0) complexes of 1-azabuta-1,3-dienes and 1-oxabuta-1,3-dienes and the application of these reactions in organic synthesis have received considerable attention. It has been shown that treatment of the 1-aza-1,3-diene complexes with methyllithium or lithium aluminium hydride leads to formation of pyrroles[1] or saturated secondary amines[2,3] respectively. When these complexes were treated with aryllithium reagents followed by triethyloxonium tetrafluoroborate the reaction lead to formation of η^4-styryl carbene complexes.[4] Treatment of the 1-oxabuta-1,3-diene complexes with alkyllithium reagents or lithium aluminium hydride leads to formation of 1,4-diketones[5] or saturated alcohols[2,3] respectively.

By contrast, examination of the literature indicates that the reaction between (1-azabuta-1,3-diene)tricarbonyliron(0) complexes and strong nitrogen-centred bases and nucleophiles is a neglected area of chemistry.

Our interest in this area was prompted by a report that treatment of (isoprene)tricarbonyliron(0) **1** with lithium diisopropylamide leads to deprotonation of the methyl group at C-2 and formation of an isoprene-equivalent anion **2** (Scheme 1).[6]



1 **2**

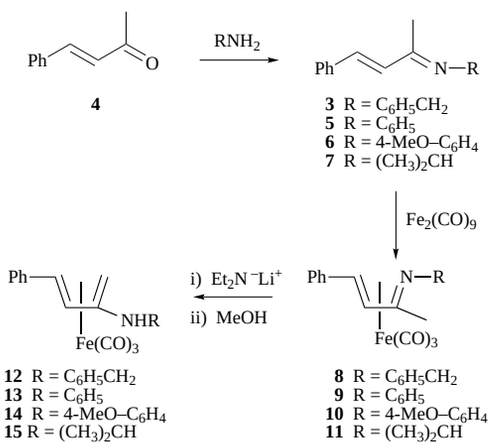
Scheme 1

This anion **2** is readily quenched by addition of alkylating agents, aldehydes or ketones and leads to the formation of an extensive range of substituted (isoprene)tricarbonyliron(0) complexes.[6]

In view of this observation and the absence of reports of the reaction between lithium amides and (2-methyl-1-azabuta-1,3-diene)tricarbonyliron(0) complexes in the literature, it was decided to initiate a study in this area. In this paper we report in detail our findings. Part of this work has been the subject of a preliminary communication.[7]

Results and discussion

Initially the reaction between the novel complex (1-benzyl-2-methyl-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) **8** and lithium diethylamide was studied. Complex **8** was synthesised as follows (Scheme 2). Equimolar amounts of benzylamine and benzylideneacetone **4** were stirred together in toluene at 60 °C for 60 h in the presence of $MgSO_4$ and activated 4 Å molecular sieves to produce a yellow mixture. This mixture was filtered to remove the solid residues and after concentration a yellow oil



4

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

12 R = $C_6H_5CH_2$
13 R = C_6H_5
14 R = 4-MeO–C_6H_4
15 R = $(CH_3)_2CH$

8 R = $C_6H_5CH_2$
9 R = C_6H_5
10 R = 4-MeO–C_6H_4
11 R = $(CH_3)_2CH$

Scheme 2

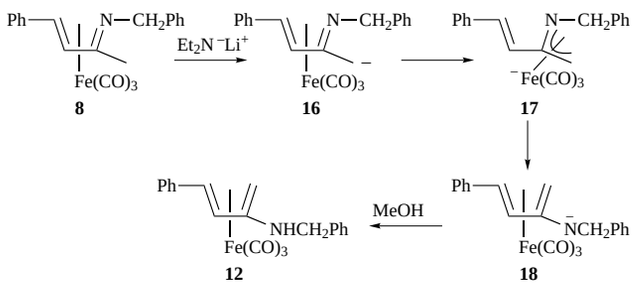
containing 1-benzyl-2-methyl-4-phenyl-1-azabuta-1,3-diene† **3** as a major constituent (>95% by 300 MHz ^{1}H NMR spectroscopy) and unreacted benzylideneacetone **4** and benzylamine (<5% by 300 MHz ^{1}H NMR spectroscopy) was isolated. There was no evidence for any other material in the reaction mixture. All attempts to isolate pure 1-benzyl-2-methyl-4-phenyl-1-azabuta-1,3-diene **3** (*i.e.* by chromatography, crystallisation or distillation) failed and resulted in either hydrolysis or polymerisation and yielded only very small quantities (<5%) of pure **3**. In view of the high yield of the initial imine forming reaction and the difficulties encountered during purification, crude **3** was used directly in the complexation reaction without further purification. Crude 1-azabuta-1,3-diene **3** and enneacarbonyldiiron(0) were added to toluene and the resulting mixture was stirred at 40 °C for 3 h under an atmosphere of nitrogen to yield a dark red mixture which upon filtration and chromatography lead to an orange oil which was chromatographed on silica to give orange crystals identified as the air stable complex **8** (50%) on the basis of their spectroscopic and analytical data.[1,8]

The reaction of complex **8** with a strong nitrogen-centred base was studied using lithium diethylamide as a representative reagent. Butyllithium was added to a solution of diethylamine in tetrahydrofuran at 0 °C and the resulting solution was stirred for 0.25 h at this temperature under an atmosphere of nitrogen. A solution of complex **8** in tetrahydrofuran was added dropwise and the resulting reaction mixture was stirred for a further 3 h at 0 °C when the reaction was quenched with methanol as a proton source. Filtration followed by chromatography lead to

† The IUPAC name for this compound is *N*-benzyl-1-methyl-3-phenylpropenylideneamine.

isolation of an orange oil which crystallised and was recrystallised to give yellow–orange crystals. These crystals gave spectroscopic and analytical data consistent with those expected from the novel enamine complex **12**. A characteristic feature of the ^{1}H NMR spectrum of **12** was the presence of a doublet at 0.57 ppm which was assigned to the highly shielded β-proton at C-1. This gave a characteristic geminal coupling (J = 4.80 Hz), to the less highly shielded α-proton at C-1 which appeared as a doublet at 1.93 ppm.[9]

The formation of enamine complex **12** may be described in terms of initial deprotonation of the methyl group at C-2 of complex **8** by the lithium diethylamide to yield the carbanionic complex **16** (Scheme 3). Rearrangement of **16** into the η^3-

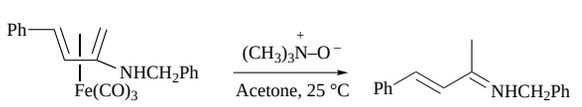


Scheme 3

azaallyl complex **17**, in which the negative charge is centred on iron, facilitates rotation of the bond between C-2 and C-3 and leads to formation of the nitrogen centred anionic homodiene complex **18** after recoordination of the π-bond between C-3 and C-4. Protonation of **18** at nitrogen upon addition of methanol leads to formation of the novel enamine complex **12**.

All attempts to reproduce this reaction using lithium diisopropylamide in tetrahydrofuran at a range of temperatures between 20 and −78 °C lead to isolation of the starting complex. There was no evidence for the rearrangement of product **12** or for the incorporation of deuterium in the methyl position of the starting 1-aza-1,3-diene complex **8** upon the addition of deuterated methanol (CD_3OD) to the reaction mixture. In view of this observation it was concluded that deprotonation of **8** does not occur when using LDA in place of lithium diethylamide. As a consequence all subsequent reactions were performed using the sterically less demanding lithium diethylamide.

Although tertiary enamine complexes of tricarbonyliron(0) in the cyclohexa-1,3-diene series have been previously synthesised,[10] compound **12** is the first example of a tricarbonyliron(0) complex of a conjugated secondary enamine. Also, oxidation of complex **12** using trimethylamine *N*-oxide results in the formation only of 1-azabuta-1,3-diene **3** (Scheme 4). This



Scheme 4

fact indicates that there is a preference for uncoordinated 1-aza-1,3-diene **3** to exist in its keto tautomer and that this novel enamine complex **12** only seems to be accessible *via* the novel deprotonation strategy described in this paper.

In order to investigate the effect of changing the nature of the substituent on nitrogen upon this novel deprotonation–rearrangement reaction, a range of tricarbonyliron(0) complexes of 2-methyl-1-azabuta-1,3-dienes derived from different primary amines were synthesised and their reactions with lithium diethylamide were studied in detail.

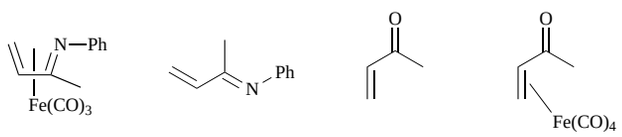
Similarly, 2-methyl-1,4-diphenyl-1-azabuta-1,3-diene **5**, obtained as a yellow solid from aniline and benzylideneacetone **4**, gave complex **9** with enneacarbonyldiiron(0).

When **9** was added to lithium diethylamide in tetrahydrofuran at 0 °C for 3 h and the reaction was quenched by addition of methanol as proton source, the novel enamine complex **13**, identified on the basis of its spectroscopic and analytical data, was obtained.

The analogous synthesis of 1-(4-methoxyphenyl)-2-methyl-4-phenyl-1-azabuta-1,3-diene **6** from *p*-anisidine and benzylideneacetone **4** and its complexation to the tricarbonyliron(0) moiety gave orange crystals of the novel complex **10**, identified on the basis of its spectroscopic and analytical data.[1,8] This complex was deprotonated (lithium diethylamide in THF) to give orange crystals of the novel enamine complex **14**.

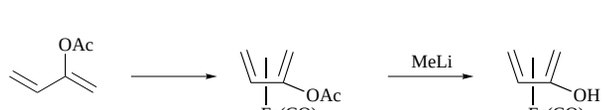
The study of this novel rearrangement reaction was extended to the complex derived from 1-isopropyl-2-methyl-4-phenyl-1-azabuta-1,3-diene **7**. This was synthesised from **4** and isopropylamine but could not be obtained as an analytically pure sample. Crude **7** and enneacarbonyldiiron(0) gave complex **11** which, with lithium diethylamide at 0 °C for 3 h followed by a proton quench, provided enamine complex **15**.

Syntheses of (enamine)tricarbonyliron(0) complexes derived from 1-azabuta-1,3-diene complexes bearing substituents in the 4-position other than a phenyl group were also attempted. Reaction of methyl vinyl ketone **21** with aniline did not give **20**



but lead to either polymerisation or preferential formation of the Michael addition product. Preformed **22**[12] from methyl vinyl ketone and enneacarbonyldiiron(0) was treated with aniline in the expectation that complexation prevents the Michael addition process. However, only the decomposition of complex **22** to methyl vinyl ketone and aniline occurred. The attempted synthesis of the (1-azabuta-1,3-diene)tricarbonyliron(0) complex derived from pent-3-en-2-one and aniline was similarly unsuccessful. These results therefore prevented a study of the effect of changing the substituent at the 4-position on rearrangement of these complexes.

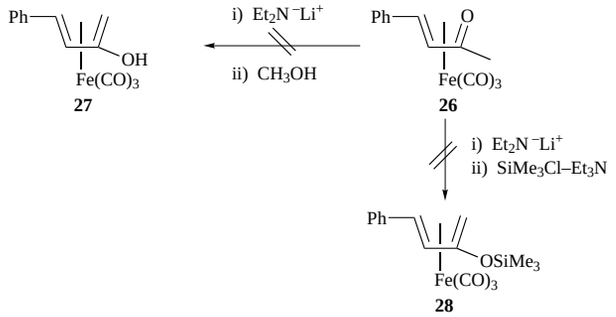
The corresponding reaction of lithium amides with (2-methyl-1-oxabuta-1,3-diene)tricarbonyliron(0) complex **26** was also investigated as a route to (enol)tricarbonyliron(0) complex **27**. Enol complexes of tricarbonyliron(0) have been previously synthesised by complexation of enol acetate **23** to the tricarbonyliron(0) moiety followed by reduction of the resulting (1,3-diene)tricarbonyliron(0) complex **24** with methyllithium to yield enol complex **25** (Scheme 5).[14]



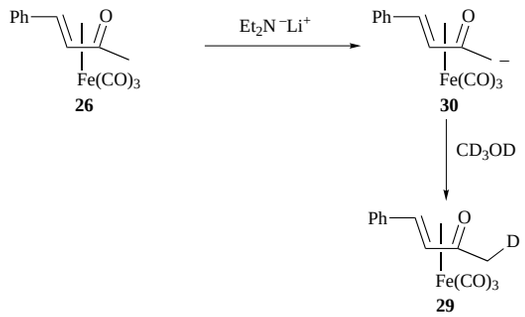
Scheme 5

(2-Methyl-4-phenyl-1-oxabuta-1,3-diene)tricarbonyliron(0) **26** and lithium diethylamide under our conditions gave only the original complex **26** and benzylideneacetone **4**. There was no evidence for the presence of enol complex **27** (Scheme 6). Similar observations were made when the reaction was quenched with trimethylsilyl chloride, when there was no evidence for the formation of the corresponding silyl enol ether complex **28**.

When the reaction between complex **26** and lithium diethylamide was quenched with deuterated methanol (CD_3OD), the ^{2}H NMR spectrum of the product mixture contained a peak at 2.55 ppm and the ^{1}H NMR spectrum showed the expected peaks for complex **26** with a significantly reduced integral of the



Scheme 6



Scheme 7

peak at 2.55 ppm due to the methyl group. These results are consistent with the presence of complex **29** which contains a deuterated methyl group (Scheme 7). Thus deprotonation at the methyl group of **26** occurs to give **30** but rearrangement into (enol)tricarbonyliron(0) complex **27** does not.

Conclusions

In conclusion it has been shown that treatment of (2-methyl-1-azabuta-1,3-diene)tricarbonyliron(0) complexes with lithium diethylamide leads to deprotonation followed by rearrangement and formation of (enamine)tricarbonyliron(0) complexes in good yield after addition of a proton source. Use of this chemistry for the synthesis of (enol)tricarbonyliron(0) complexes from (2-methyl-1-oxabuta-1,3-diene)tricarbonyliron(0) complexes was unsuccessful, although deuteration experiments show that deprotonation of the methyl group does occur.

Experimental

All reactions under an atmosphere of nitrogen were performed using standard vacuum and Schlenk line techniques.[15] Diethyl ether was dried over lithium aluminium hydride and was distilled, toluene was dried over sodium metal and was distilled and tetrahydrofuran was dried over potassium benzophenone ketyl and was distilled. Light petroleum refers to the fraction boiling in the range 40–60 °C. Diethylamine was redistilled and butyllithium was used as a 1.6 M solution in hexanes. Melting points were recorded on a Kofler hot stage micromelting point apparatus and are uncorrected. ^{1}H NMR 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 ppm relative to a tetramethylsilane standard. Chromatography was performed on Merck (40–63 μm) silica. Filtrations through alumina were performed using deactivated Brockmann (grade iv) alumina. Elemental analyses were performed on a Leeman Laboratories CE 477 instrument.

Preparation of (1-benzyl-2-methyl-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) 8

Benzylideneacetone **4** (1.00 g, 6.84 mmol) and benzylamine (0.73 g, 6.84 mmol) were dissolved in toluene (5 ml) and the resulting solution was stirred at 60 °C for 60 h under an atmosphere of nitrogen. The reaction mixture was dried over $MgSO_4$ and the solvent was removed under reduced pressure to leave a yellow oil identified as containing 1-benzyl-2-methyl-4-phenyl-1-azabuta-1,3-diene **3** as a major constituent (<80%) on the basis of its ^{1}H NMR spectrum, δ_H(300 MHz; $CDCl_3$) 2.16 (3H, s, CH_3), 4.66 (2H, s, CH_2Ph), 6.96 (1H, d, *J* 16.6, PhCH=C*H*), 7.06 (1H, d, *J* 16.6, PhC*H*=CH) and 7.21–7.54 (10H, m, 2 × Ph). In view of the difficulty experienced in the purification of 1-azabuta-1,3-diene **3** the crude product mixture was used directly in the complexation step without further purification. Enneacarbonyldiiron(0) (4.98 g, 13.68 mmol) and toluene (20 ml) were added to crude **3** and the resulting mixture was heated to 40 °C for 3 h under an atmosphere of nitrogen. The resulting dark mixture was filtered through alumina to remove the solid residues and the solvent removed under reduced pressure to yield a red gum. This gum was chromatographed on silica using diethyl ether–hexane (1:2) as the eluent to yield red crystals identified as complex **8** on the basis of their spectroscopic and analytical data (1.28 g, 50%), mp 95–97 °C (Found: C, 63.98; H, 4.45; N, 3.64; $C_{20}H_{17}FeNO_3$ requires C, 63.99; H, 4.57; N, 3.73%); ν_{max}(hexane/cm^{-1} 2050s (C≡O), 1988s (C≡O) and 1965s (C≡O); δ_H(300 MHz; $CDCl_3$) 2.45 (3H, s, CH_3), 2.92 (1H, d, *J* 8.7, PhC*H*), 3.41 (1H, d, *J* 15.4, NC*H*HPh), 4.03 (1H, d, *J* 15.4, NCH*H*Ph), 5.43 (1H, d, *J* 8.7, PhCH=C*H*), 7.12–7.37 (10H, m, 2 × Ph); δ_C(75 MHz; $CDCl_3$) 15.25 (*C*H_3), 58.18 (Ph*C*H=), 58.49 (Ph*C*H_2N), 70.33 (PhCH=*C*H), 126.12, 126.54, 127.07, 127.86, 128.29, 128.48, 129.83, 140.00, 140.19 (2 × Ph and *C*=N); *m*/*z* 361 (M^+, 5%), 347 (25, M − CO), 319 (45, M − 2CO) and 291 (100, M − 3CO).

Reaction of (1-benzyl-2-methyl-4-phenyl-1-azabuta-1,3-diene)-tricarbonyliron(0) 8 with lithium diethylamide

Butyllithium solution (1.6 M; 0.43 ml, 0.7 mmol) was added to a solution of diethylamine (0.067 ml, 0.65 mmol) in tetrahydrofuran (3 ml) at 0 °C and the resulting solution was stirred at this temperature for 0.25 h under an atmosphere of nitrogen. A solution of (1-benzyl-2-methyl-4-phenyl-1-azabuta-1,3-diene)-tricarbonyliron(0) **8** (0.05 g, 0.13 mmol) in tetrahydrofuran (4 ml) was added and the resulting solution was stirred at 0 °C for 3 h under an atmosphere of nitrogen. The reaction was quenched with methanol (0.05 ml) and the resulting mixture was allowed to warm up to room temperature for 0.5 h. The orange mixture produced was filtered through a plug of alumina to remove the solid residues and the solvent was removed under reduced pressure to yield an orange–brown gum. This gum was chromatographed on silica using hexane–diethyl ether (3:1) as the eluent to yield yellow crystals identified as (2-benzylamino-4-phenylbuta-1,3-diene)tricarbonyliron(0) **12** on the basis of their spectroscopic and analytical data (0.03 g, 60%), mp 59–61 °C (Found: C, 64.01; H, 4.46; N, 3.72. $C_{20}H_{17}FeNO_3$ requires C, 63.99; H, 4.57; N, 3.73%); ν_{max}(thin film)/cm^{-1} 3409m (NH), 2034vs (C≡O) and 1995vs (C≡O); δ_H(300 MHz; $CDCl_3$) 0.57 (1H, d, *J* 4.8, =CH_β), 1.84 (1H, d, *J* 8.1, PhC*H*=CH), 1.93 (1H, dd, *J* 1.6 and 4.8, =CH_α), 3.51 (1H, br, N*H*CH_2Ph), 4.19 (1H, d, *J* 13.2, NHC*H*HPh), 4.36 (1H, d, *J* 13.2, NHCH*H*Ph), 5.24 (1H, dd, *J* 8.1 and 1.6, PhCH=C*H*), 7.10–7.42 (10H, m, 2 × Ph); δ_C(75 MHz; $CDCl_3$) 32.02 (C=*C*H_2), 49.08 (NH*C*H_2Ph), 54.47 (Ph*C*H=CH), 62.22 (PhCH=*C*H), 125.73, 126.07, 126.48, 127.69, 128.02, 128.42, 128.91, 137.60 and 141.61 (2 × Ph and *C*=CH_2); *m*/*z* (EI) 375 (10%, M^+).

Synthesis of (2-methyl-1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) 9

Benzylideneacetone **4** (1.00 g, 6.85 mmol) and aniline (0.68 g, 6.85 mmol) were dissolved in toluene (5 ml) and the resulting solution was stirred at 25 °C for 96 h under an atmosphere of nitrogen. Analysis of the reaction mixture by ^{1}H NMR spectroscopy indicated that 2-methyl-1,4-diphenyl-1-azabuta-1,3-diene **5** was present as the major reaction product (>70%).[1]

Toluene (10 ml) and enneacarbonyldiiron(0) (4.99 g, 13.70 mmol) were added to crude **5** and the resulting mixture was stirred at 40 °C for 3 h under an atmosphere of nitrogen. The resulting dark mixture was filtered through a plug of alumina to remove the iron residues and the solvent was removed under reduced pressure to yield a dark red gum. This gum was chromatographed on silica using hexane–diethyl ether (10:1) as the eluent to yield red crystals identified as complex **9** (1.98 g, 80%) by comparison of their spectroscopic data with data quoted in the literature.[1]

Reaction of (2-methyl-1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) 9 with lithium diethylamide

Butyllithium solution (1.6 M; 2.20 ml, 3.50 mmol) was added to a solution of diethylamine (0.36 ml, 3.46 mmol) in tetrahydrofuran (6 ml) at 0 °C and the resulting solution was stirred at this temperature for 0.25 h under an atmosphere of nitrogen. A solution of (2-methyl-1,4-diphenyl-1-azabuta-1,3-diene)-tricarbonyliron(0) **9** (0.25 g, 0.69 mmol) in tetrahydrofuran (9 ml) was added and the resulting solution was stirred at 0 °C for 3 h under an atmosphere of nitrogen. The reaction was quenched with methanol (0.05 ml) and the resulting mixture was allowed to warm up to room temperature for 0.5 h. The orange mixture produced was filtered through a plug of alumina to remove the solid residues and the solvent was removed under reduced pressure to yield an orange–brown gum. This gum was chromatographed on silica using hexane–diethyl ether (3:1) as the eluent to yield a yellow oil which crystallised on standing. These crystals were identified as (2-phenylamino-4-phenylbuta-1,3-diene)tricarbonyliron(0) **13** on the basis of their spectroscopic and analytical data (0.14 g, 55%), mp 132–135 °C (Found: C, 62.89; H, 3.98; N, 3.81. $C_{19}H_{15}FeNO_3$ requires C, 63.18; H, 4.19; N, 3.88%); ν_{max}(thin film)/cm^{-1} 2042s (C≡O) and 1976s (br) (C≡O); δ_H(300 MHz; $CDCl_3$) 0.76 (1H, d, *J* 4.6, =CH_β), 1.82 (1H, d, *J* 8.1, PhC*H*=), 2.20 (1H, dd, *J* 1.7 and 4.6, =CH_α), 5.30 (1H, br, N*H*), 5.63 (1H, dd, *J* 8.1 and 1.7, PhCH=C*H*), 7.11–7.40 (10H, m, 2 × Ph); δ_C(75 MHz; $CDCl_3$) 34.55 (=*C*H$_2$), 54.33 (Ph*C*H=), 65.03 (PhCH=*C*H), 121.05, 121.21, 123.45, 125.91, 126.13, 128.47, 129.54, 140.69 and 141.41 (2 × Ph and *C*=CH$_2$); *m*/*z* 361 (M$^+$, 15%), 333 (35, M − CO), 305 (25, M − 2CO) and 277 (100, M − 3CO).

Preparation of 1-(4-methoxyphenyl)-2-methyl-4-phenyl-1-azabuta-1,3-diene 6

4-Anisidine (4-methoxyaniline) (6.21 g, 0.05 mmol) was added to a solution of benzylideneacetone **4** (7.31 g, 0.05 mmol) in toluene (20 ml) and the resulting solution was heated at reflux over 4 Å molecular sieves for 60 h to give a dark mixture. The solid residues were removed by filtration and the solvent was removed under reduced pressure to yield a dark oil which crystallised on standing. The resulting material was recrystallised from ethanol to yield 1-(4-methoxyphenyl)-2-methyl-4-phenyl-1-azabuta-1,3-diene **6** as yellow crystals (2.99 g, 24%), mp 82–84 °C (Found: C, 81.33; H, 6.80; N, 5.56. $C_{17}H_{17}NO$ requires C, 81.25; H, 6.82; N, 5.57%); ν_{max}/cm^{-1} 1632m (C=C) and 1575m (C=N); δ_H(300 MHz; $CDCl_3$) 2.10–2.44 (3H, s, CH_3), 3.81 (3H, s, OCH_3) and 6.73–7.55 (11H, m, 2 × Ph and PhC*H*=C*H*); δ_C(75 MHz; $CDCl_3$) 15.82 (*C*H$_3$), 55.41 (O*C*H$_3$), 114.10, 121.10, 127.31, 127.45, 128.81, 128.96, 131.99, 135.94, 136.90, 144.25, 156.06, 166.27 (2 × Ph and Ph*C*H=CH*C*=N); *m*/*z* (FAB) 251 (M$^+$, 50%) and 148 (100, M − PhCH=CH).

Preparation of [1-(4-methoxyphenyl)-2-methyl-4-phenyl-1-azabuta-1,3-diene]tricarbonyliron(0) 10

Enneacarbonylidiiron(0) (2.91 g, 8.00 mmol) and 1-(4-methoxyphenyl)-2-methyl-4-phenyl-1-azabuta-1,3-diene **6** (1.00 g, 3.98 mmol) were stirred in toluene (10 ml) at 40 °C for 3 h under an atmosphere of nitrogen to give a dark mixture. This mixture was cooled to room temperature and was filtered through a plug of alumina to give a deep red solution. The solvent was removed under reduced pressure to give a dark red solid which was chromatographed on silica using light petroleum–ethyl acetate (10:1) as the eluent to yield [1-(4-methoxyphenyl)-2-methyl-4-phenyl-1-azabuta-1,3-diene]tricarbonyliron(0) **10** as red crystals (1.44 g, 92%), mp 110–111 °C (decomp.) (Found: C, 61.17; H, 4.40; N, 3.58. $C_{20}H_{17}FeNO_4$ requires C, 61.41; H, 4.38; N, 3.58%), ν_{max}(nujol)/cm^{-1} 2049s (C≡O), 1991s (C≡O) and 1977s (C≡O); δ_H(300 MHz; $CDCl_3$) 2.40 (3 H, s, CH_3), 3.22 (1H, d, *J* 8.5, PhC*H*=CH), 3.76 (3H, s, CH_3), 5.52 (1H, d, *J* 8.5, PhCH=C*H*) and 6.67–7.32 (9H, m, 2 × Ph); δ_C(75 MHz; $CDCl_3$) 16.59 (*C*H$_3$), 55.49 (O*C*H$_3$), 59.61 (Ph*C*H=CH), 70.83 (PhCH=*C*H), 125.61 (=CH*C*CH$_3$), 114.06, 123.65, 126.52, 126.67, 128.64, 143.23 and 154.75 (2 × Ph and *C*=N); *m*/*z* (FAB) 460 (20%, M + 69), 363 (10, M − CO), 335 (20, M − 2CO) and 307 (100, M − 3CO).

Reaction of [1-(4-methoxyphenyl)-2-methyl-4-phenyl-1-azabuta-1,3-diene]tricarbonyliron(0) 10 with lithium diethylamide

Butyllithium solution (1.6 M; 3.22 ml, 2.01 mmol) was added to a solution of diethylamine (0.23 g, 3.20 mmol) in tetrahydrofuran (3 ml) at 0 °C and the resulting solution was stirred at this temperature for 0.25 h under an atmosphere of nitrogen. A solution of [1-(4-methoxyphenyl)-2-methyl-4-phenyl-1-azabuta-1,3-diene]tricarbonyliron(0) **10** (0.25 g, 0.64 mmol) in tetrahydrofuran (4 ml) was added and the resulting solution was stirred at 0 °C for 3 h under an atmosphere of nitrogen. The reaction was quenched with methanol (0.05 ml) and the resulting mixture was allowed to warm up to room temperature for 0.5 h. The orange mixture produced was filtered through a plug of alumina to remove the solid residues and the solvent was removed under reduced pressure to yield an orange–brown gum. This gum was chromatographed on silica using hexane–diethyl ether (3:1) as the eluent to yield yellow crystals identified as **14**, [2-(4-methoxyphenylamino)-4-phenylbuta-1,3-diene]tricarbonyliron(0), on the basis of their spectroscopic and analytical data (0.11 g, 41%), mp 132–133 °C (Found: C, 61.43; H, 4.38; N, 3.59. $C_{20}H_{17}FeNO_4$ requires C, 61.41; H, 4.38; N, 3.58%); ν_{max}(nujol)/cm^{-1} 2049s (C≡O), 1991s (C≡O) and 1977s (C≡O); δ_H(300 MHz; $CDCl_3$) 0.67 (1H, d, *J* 4.8, =CH_β), 1.84 (1H, d, *J* 8.1, PhC*H*), 2.06 (1H, dd, *J* 1.7 and 4.8, =CH_α), 3.64 (3H, s, OCH_3), 5.06 (1H, br, N*H*), 5.39 (1H, d, *J* 8.1 and 1.7, PhCH=C*H*) and 6.94–7.26 (9H, 2 × Ph); δ_C(75 MHz; $CDCl_3$) 32.48 (C=*C*H$_2$), 54.53 (Ph*C*H=), 55.49 (O*C*H$_3$), 63.42 (PhCH=*C*H), 114.79, 124.35, 125.16, 125.76, 126.07, 128.39, 132.61, 141.66, 156.69 (2 × Ph and *C*=CH$_2$); *m*/*z* 391 (M$^+$, 7%), 363 (25, M − CO), 335 (20, M − 2CO) and 307 (100, M − 3CO).

Preparation of (1-isopropyl-2-methyl-4-phenyl-1-azabuta-1,3-diene)tricarbonyliron(0) 11

Benzylideneacetone **4** (0.30 g, 2.05 mmol) and isopropylamine (0.12 g, 2.05 mmol) were dissolved in toluene (5 ml) and the resulting solution was stirred at 25 °C for 96 h. The reaction mixture was dried over $MgSO_4$ and the solvent was removed under reduced pressure to leave a yellow oil identified as containing 1-isopropyl-2-methyl-4-phenyl-1-azabuta-1,3-diene **7** as a major constituent (<80%) on the basis of its ^{1}H NMR and ^{13}C NMR spectra, δ_H(300 MHz; $CDCl_3$) 1.18 [6H, d, *J* 6.2, CH(CH_3)$_2$], 2.04 (3H, s, CH_3), 3.79 [1H, septet, *J* 6.2, C*H*(CH$_3$)$_2$], 6.86 (1H, d, *J* 16.6, PhCH=C*H*), 6.95 (1H, d, *J* 16.6, PhC*H*=CH) and 7.21–7.69 (2 × Ph); δ_C(300 MHz; $CDCl_3$) 12.66 [CH(*C*H$_3$)$_2$], 23.28 (*C*H$_3$), 50.50 [*C*H(CH$_3$)$_2$], 126.59, 128.11, 128.35, 132.89, 134.18 (2 × Ph and PhCH=*C*H), 136.01 (Ph*C*H=) and 162.59 (*C*=N). In view of the difficulty experienced during the isolation of **7** the crude material was used directly in the complexation reaction without further purification. Enneacarbonyldiiron(0) (4.98 g, 13.68 mmol) was added to a solution of crude **7** in toluene and the resulting mixture was heated at 40 °C for 3 h to yield a dark mixture. This mixture was

filtered to remove the iron residues and the solvent was removed under reduced pressure to give a dark red gum. This gum was chromatographed on silica using diethyl ether–hexane (1:2) as the eluent to yield red crystals identified as complex **11** on the basis of their spectroscopic and analytical data (0.21 g, 31%), mp 92–94 °C (Found: C, 58.44; H, 5.18; N, 4.30. $C_{16}H_{17}FeNO_3$ requires C, 58.74; H, 5.24; N, 4.28%); ν_{max}(thin film)/cm^{-1} 2047s (C≡O), 1994s (C≡O), 1964s (C≡O) and 1562m (C=N); δ_H(300 MHz; $CDCl_3$) 1.08 (3H, d, *J* 6.1, CHCH_3), 1.18 (3H, d, *J* 6.1, CHCH_3), 2.38 (3H, s, CH_3), 2.58 [1H, m, C*H*(CH_3)$_2$], 2.90 (1H, d, *J* 8.8, PhC*H*=), 5.33 (1H, d, *J* 8.8, PhCH=C*H*) and 7.09–7.27 (5H, m, Ph); δ_C(75 MHz; $CDCl_3$) 14.90 (*C*H$_3$), 23.83 (CH*C*H$_3$), 27.04 (CH*C*H$_3$), 52.46 [*C*H(CH$_3$)$_2$], 58.95 (Ph*C*H=), 69.98 (PhCH=*C*H), 126.11, 126.50, 127.76, 128.46 and 140.00 (Ph and *C*=N); *m*/*z* 299 (33, M − CO), 271 (80, M − 2CO) and 243 (100, M − 3CO).

Reaction of (1-isopropyl-2-methyl-4-phenyl-1-azabuta-1,3-diene)-tricarbonyliron(0) 11 with lithium diethylamide

Butyllithium solution (1.6 M; 1.31 ml, 2.10 mmol) was added to a solution of diethylamine (0.15 g, 2.06 mmol) in tetrahydrofuran (3 ml) at 0 °C and the resulting solution was stirred at this temperature for 0.25 h under an atmosphere of nitrogen. A solution of (1-isopropyl-4-phenyl-1-azabuta-1,3-diene)-tricarbonyliron(0) **11** (0.14 g, 0.41 mmol) in tetrahydrofuran (4 ml) was added and the resulting solution was stirred at 0 °C for 3 h under an atmosphere of nitrogen. The reaction was quenched with methanol (0.05 ml) and the resulting mixture was allowed to warm up to room temperature for 0.5 h. The orange mixture produced was filtered through a plug of alumina to remove the solid residues and the solvent was removed under reduced pressure to yield an orange–brown gum. This gum was chromatographed on silica using hexane–diethyl ether (3:1) as the eluent to yield yellow crystals identified as (2-isopropyl-amino-4-phenylbuta-1,3-diene)tricarbonyliron(0) **15** (0.06 g, 45%), on the basis of their spectroscopic and analytical data, mp 49–50 °C (Found: C, 58.70; H, 5.28; N, 4.29. $C_{16}H_{17}FeNO_3$ requires C, 58.73; H, 5.24; N, 4.28%); ν_{max}(thin film)/cm^{-1} 3418br (NH), 2051s (C≡O) and 1951s (C≡O); δ_H(300 MHz; $CDCl_3$) 0.48 (1H, d, *J* 4.5, =CH_β), 1.26 (3H, d, *J* 6.3, NCHCH_3), 1.31 (3H, d, *J* 6.3, NCHCH_3), 1.80 (1H, m, =CH_α), 1.84 (1H, d, *J* 7.7, PhC*H*=CH), 3.24 (1H, br, N*H*), 3.61 [1H, m, C*H*(CH$_3$)$_2$], 5.12 (1H, d, *J* 7.7, PhCH=C*H*) and 7.07–7.27 (5H, m, Ph); δ_C(75 MHz; $CDCl_3$) 22.19 (CH*C*H$_3$), 23.67 (CH*C*H$_3$), 30.86 (=*C*H$_2$), 44.66 [*C*H(CH$_3$)$_2$], 54.53 (Ph*C*H=), 60.65 (PhCH=*C*H), 125.56, 126.03, 127.44, 128.37 and 142.34 (Ph and *C*=CH$_2$).

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