# The chemistry of (1-azabuta-1,3-diene)tricarbonyliron(0) complexes

Timothy N. Danks [a,b,*], Gabriele Wagner [a,*]

[a] *Chemistry Division, SBMS, University of Surrey, Guildford, Surrey GU2 7XH, UK*
[b] *The Oratory School, Woodcote, Reading, Berkshire RG8 0PJ, UK*

## Abstract

In this review, an overview of synthetic and structural aspects of 1-azabuta-1,3-diene complexes of iron is given and the reactivity of these complexes is discussed with regard to inorganic, organometallic, organic and stereochemical aspects of their chemistry. Their application in the synthesis of organic and organometallic target compounds, or as transfer reagents of the tricarbonlyiron(0) moiety is demonstrated.
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## 1. Introduction

Ligands that are π-bound to organometallic moieties play an important role in organometallic chemistry and organic synthesis. Most prominent examples are found in areas such as ferrocene chemistry, benzene tricarbonylchromium chemistry or chemistry of complexes bearing a tricarbonyliron(0) moiety. Among these, 1,3-diene, 1-oxabuta-1,3-diene or 1-azabuta-1,3-diene complexes are most common. Unlike their homo-1,3-diene analogues, which were first synthesised in 1930 and whose chemistry is well established and extensively reviewed [1,2], the 1-azabuta-1,3-diene complexes are known since 1967 only [3], but have attracted significant attention in recent years. This review will present an overview of the synthesis, structure and reactivity of 1-azabuta-1,3-diene complexes of iron and cover the inorganic, organometallic and organic aspects of their chemistry, as well as their utilisation in synthetic organic chemistry.
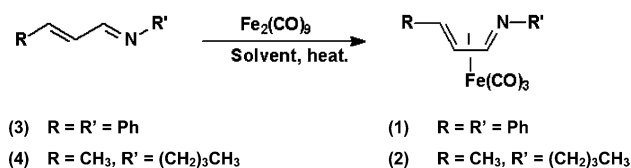
## 2. Synthesis

### 2.1. From α,β-unsaturated imines and iron carbonyls

The first reported synthesis of (1-azabuta-1,3-diene)tricarbonyliron(0) complexes (**1**) and (**2**) appeared in 1967 when 1-azabuta-1,3-dienes (**3**) and (**4**) (derived from crotonaldehyde or cinnamaldehyde) were heated with diironnonacarbonyl or triirondodecacarbonyl in an inert solvent such as benzene (Scheme 1) [3]. The resulting complexes **1** and **2** were isolated as air stable, orange-red crystalline solids in yields in excess of 80%.

The reaction is quite generally applicable and a large variety of complexes have been prepared from stable, isolated precursor 1-azabuta-1,3-dienes [4–7]. In cases where isolation of the starting 1-azabuta-1,3-diene is problematic [e.g. **6**–**8**], reaction of the crude ligand mixture with a source of the tricarbonyliron(0) moiety [usually $Fe_2(CO)_9$] leads to complexes **9**–**11** in good yields (Scheme 2) [5,8]. In these examples, the formation of the intermediate 1-azabuta-1,3-dienes (**6**)–(**8**) was observed by ^{1}H NMR spectroscopy but attempted isolation resulted in their decomposition.

* Corresponding authors. Tel.: +1483-686831; fax: +1483-686851.
*E-mail addresses:* t.danks@oratory.co.uk (T.N. Danks), g.wagner@surrey.ac.uk (G. Wagner).
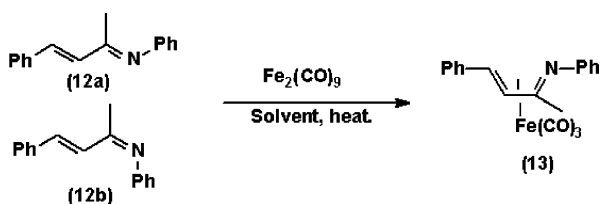
Scheme 1.
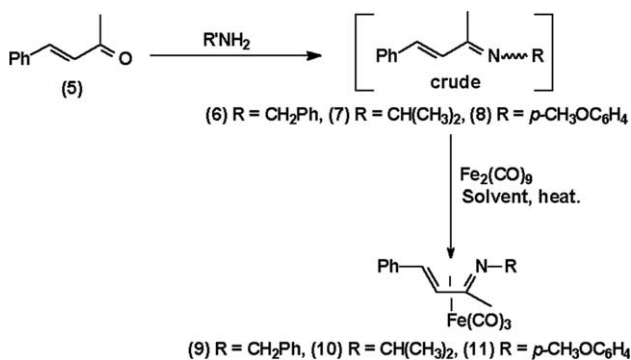


Scheme 2.

In the synthesis of 1-azabuta-1,3-dienes bearing a substituent other than H at C-2 (e.g. **12**), a mixture of $E,E_{(C=N)}$ (**12a**) and $E,Z_{(C=N)}$ (**12b**) geometrical isomers is usually formed. Complexation of the 1-azabuta-1,3-diene mixture (**12**) to the tricarbonyliron(0) moiety by reaction with Fe$_2$(CO)$_9$ leads to complex **13** in which the $E,E_{(C=N)}$ ligand is selectively coordinated to the tricarbonyliron(0) moiety (Scheme 3) [4]. Evidence for the stereochemistry of the ligand was obtained from NOE difference spectroscopy. Irradiation into the signal of the methyl group leds to an enhancement of the signal of the *ortho* protons of the *N*-Ph. On the other hand, irradiation of the signal due to the *ortho* protons of the *N*-Phenyl did not produce an enhancement of the signals due to the proton at C-4. Such a signal would be expected if the $E,Z_{(C=N)}$ was complexed to the tricarbonyliron(0) moiety. The selective complexation of the $E,E_{(C=N)}$ to the tricarbonyliron(0) moiety was attributed to steric factors. In the case of the $E,Z_{(C=N)}$ complex, there is a significant interaction between the *ortho* protons of the *N*-phenyl and the proton at C-4 of the 1-azabuta-1,3-diene and this presumably prevents the complexation reaction. When the tricarbonyliron(0)

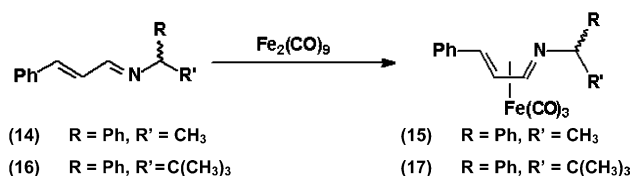moiety is removed from the complex by mild oxidation [(CH$_3$)$_3$N$^+$–O$^-$], the 1-azabuta-1,3-diene reverts to the original mixture of geometric isomers [4–6] and **12a** and **12b** are regenerated.

1-Azabuta-1,3-dienes containing chiral groups at nitrogen have also been coordinated to the tricarbonyliron(0) moiety and this leads to the formation of diastereomeric complexes. For example, reaction of diironnonacarbonyl with 1-azabuta-1,3-dienes (**14**) and (**16**) derived from cinnamaldehyde and α-substituted benzylamines produces the diastereomeric complexes **15** and **17**, respectively (Scheme 4) [4,9]. When the α-substituent R of the azabuta-1,3-diene is a methyl group, a 1:1 mixture of diastereoisomers is formed. However, when R is a *tert*-butyl group formation of a 94:6 ratio of diastereoisomers is observed, showing the influence of steric factors on the stereoselectivity with which the complexation occurs. Nuclear Overhauser enhancement difference spectroscopy has been used to identify the relative stereochemistry of both major and minor diastereoisomers. Similar results have been observed for the complexes derived from α-substituted ethylamines [7].
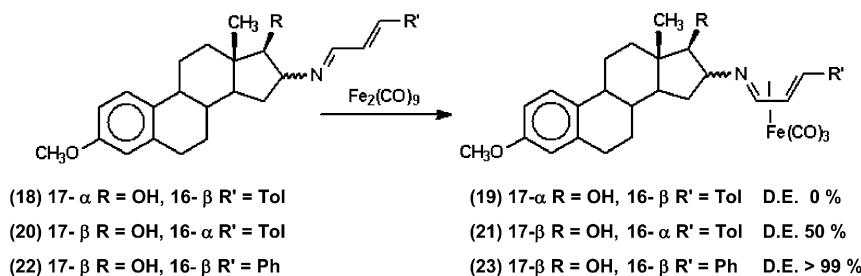
More recently steroidal imines have been complexed to the tricarbonyliron(0) moiety using ligands derived from 16-amino steroids and cinnamaldehyde (Scheme 5) [10]. The diastereoselectivity of these reactions was shown to be highly dependent on the steric demands of the neighbouring group in the 17-position and the relative configurations of the substituents. Results illustrate that the best d.e. is obtained for complex **23**, where the substituents at C-16 and C-17 are both in the β-position.

For complex **24** derived from the 17-β amino steroid and cinnamaldehyde, a crystal structure has been obtained (Figs. 1 and 2) [10]. It shows clearly the stereochemistry of the product obtained and illustrates the η$^4$-binding mode of the tricarbonyliron(0) moiety and its position on the sterically less hindered side of the ligand.

Sonochemistry has been shown to have beneficial effects in the synthesis of (1-azabuta-1,3-diene)tricarbonyliron(0) complexes, and this technique was also successfully employed for synthesis of diastereomeric complexes [11]. For example, reaction of the 1-azabuta-1,3-dienes derived from phenylglycinol and cinnamaldehyde and 1-phenylethylamine and 4-methoxybenzylidene



Scheme 3.



Scheme 4.

(18) 17-α R = OH, 16-β R' = Tol

(20) 17-β R = OH, 16-α R' = Tol

(22) 17-β R = OH, 16-β R' = Ph

(19) 17-α R = OH, 16-β R' = Tol   D.E.  0 %

(21) 17-β R = OH, 16-α R' = Tol   D.E. 50 %

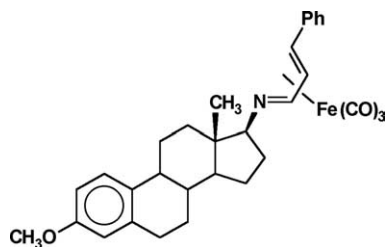(23) 17-β R = OH, 16-β R' = Ph   D.E. > 99 %
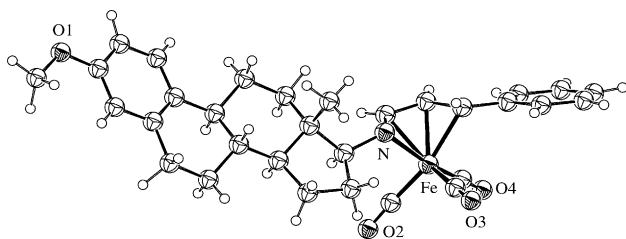
Scheme 5.



Fig. 1. Compound 24.



Fig. 2. Crystal structure of 24 [10].

acetone results in the formation of diastereomeric complexes, which can be separated by chromatography at low temperature.

Both 1-azabuta-1,3-diene and iron carbonyl moiety can be varied to quite some extent. Thus, diastereomeric complexes derived from chiral α,β-unsaturated hydrazones have been synthesised in high d.e. by direct complexation of the chiral ligand to the tricarbonyliron(0) moiety using diironnonacarbonyl [12]. Complexes 25 and 26, from a proline derived ligand, are illustrated as examples (Fig. 3).

Synthesis of diastereomeric complexes by photolysis of a pre-formed substituted iron carbonyl and a chiral 1-azabuta-1,3-diene ligand has also been reported [13]. For example, reaction of Fe(CO)$_4$PPh$_3$ with R-1-
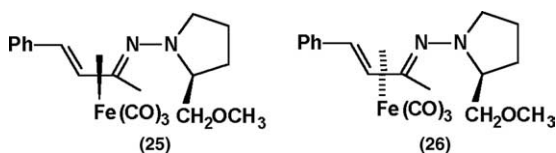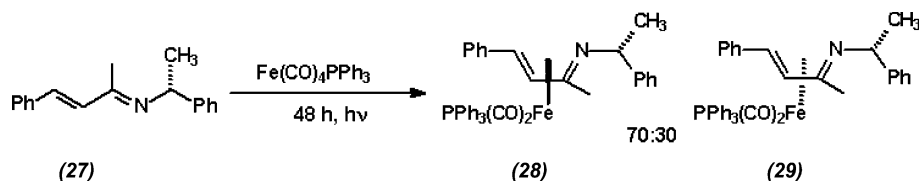


Fig. 3.

(1-phenylethyl)-2-methyl-4-phenyl-1-azabuta-1,3-dienes (27) under photochemical conditions leads to the formation of R,R and R,S complexes 28 and 29 (Scheme 6). Subsequent separation of the diastereoisomers led to the isolation of the first homochiral 1-azabuta-1,3-diene complexes. Single crystal X-ray analysis confirmed the proposed structures.
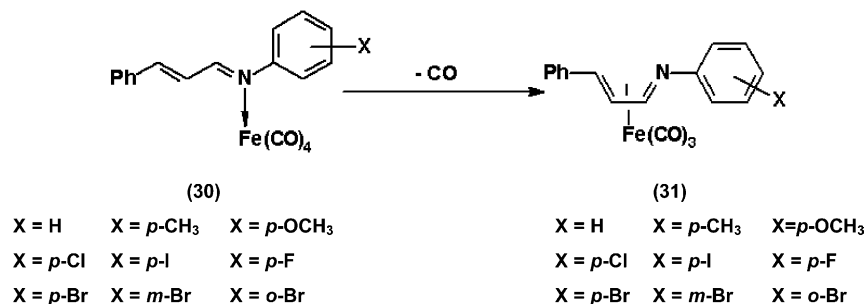
The kinetics and mechanism of the complexation reaction has been studied extensively [14]. Initial reaction of Fe$_2$(CO)$_9$ with a 1-azabuta-1,3-diene has been shown to lead to the formation of intermediate complexes 30 [15]. In these complexes, the 1-azabuta-1,3-diene is co-ordinated to the tetracarbonyliron(0) moiety via the nitrogen lone pair (σ-N complex). In many cases, these intermediates have been isolated and partially characterised [15]. When these complexes are warmed, a carbonyl ligand is lost and formation of the tricarbonyliron(0) complexes 31 is observed (Scheme 7).

The mechanism and kinetics for the conversion of the σ-N-tetracarbonyliron(0) complexes (30) into the (1-azabuta-1,3-diene)tricarbonyliron(0) complexes (31) was the subject of detailed studies. The reaction, as expected, is first order with respect to the complex. When the reaction is performed under an atmosphere of carbon monoxide, the product mixture consists of mainly Fe(CO)$_5$ and the free 1-azabuta-1,3-diene ligand. Also when PPh$_3$ is added to complexes 30, the major reaction product is (PPh$_3$)$_2$(CO)$_3$Fe. There was no evidence for a carbonyl substituted 1-azabuta-1,3-diene complex, which reflects the high reactivity of the weakly bound σ-N-tetracarbonyliron(0) complexes (30).
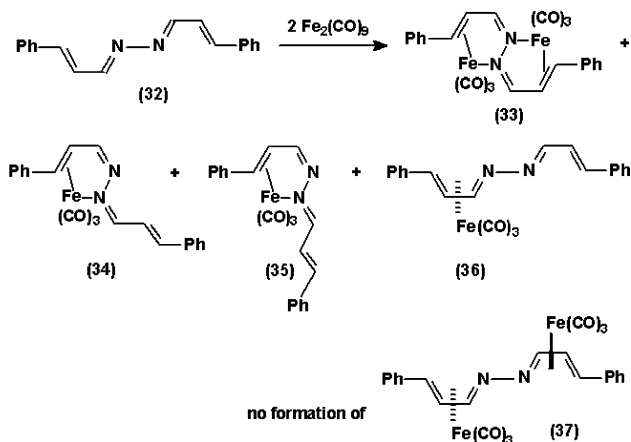
The reaction of 1-azabuta-1,3-dienes with iron carbonyls reaches its limitations when azine (2,3-diazabutadienes)-derived compounds are used, because such ligands tend to undergo cleavage of the N–N bond, or ortho proton rearrangement to the azomethine carbon and metalation of the phenyl ring [16]. In the reaction of N,N'-bis(3-phenylallylidene)hydrazine (32) with Fe$_2$(CO)$_9$, however, the complex 33 is produced in which the ligand binds to the metal through η$^2$-alkene and σ-N coordination to the more remote nitrogen atom (Scheme 8) [17]. As intermediates, compounds 34, 35 and 36 were detected and structurally characterised. The presence of 36 indicates that 32 can also undergo

Scheme 6.



(30)

| X = H | X = p-CH₃ | X = p-OCH₃ |
|-------|-----------|------------|
| X = p-Cl | X = p-I | X = p-F |
| X = p-Br | X = m-Br | X = o-Br |

(31)

| X = H | X = p-CH₃ | X=p-OCH₃ |
|-------|-----------|----------|
| X = p-Cl | X = p-I | X = p-F |
| X = p-Br | X = m-Br | X = o-Br |

Scheme 7.



Scheme 8.

$\eta^4$-coordination, although with a lower preference. Thus, complex **37** bearing two $\eta^4$-coordinated tricarbonyliron moieties was not formed.

Aromatic imines can be considered as 1-azabuta-1,3-dienes in which the C=C bond is part of the aromatic ring system. Typically, these compounds react with Fe₂(CO)₉ under CH activation and formation of dinuclear or trinuclear complexes, many of which were characterised by X-ray crystallography [18–26], and some of
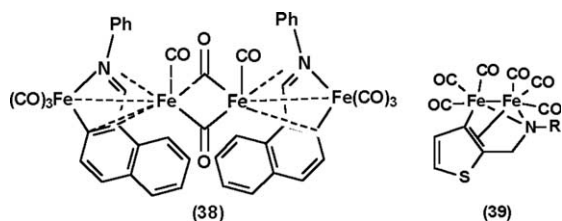


Fig. 4.

which are shown in Fig. 4. Only in the case of a naphthylimine, a mononuclear 1-azabuta-1,3-diene complex in which an aromatic C=C bond is involved in coordination was detected as a by-product in minor quantity [26].

Prolonged heating of the 1-azabuta-1,3-dienes with excess Fe₂(CO)₉ equally leads to the formation of a di-iron cluster **40** [27]. Formation of **40** arises from reaction of the 1-azabuta-1,3-diene complex **1** with the Fe(CO)₅ produced from Fe₂(CO)₉ during the initial complexation reaction and may be considered as involving H transfer from position 4 of the 1-azabuta-1,3-diene to the 2-position and formation of an Fe–C σ-bond.

This reactivity of (1-azabuta-1,3-diene)tricarbonyl-iron(0) complexes towards transition metal carbonyls can be used for the synthesis of hetero-bimetallic clusters [28]. Thus, compounds **41** and **42** were prepared by reaction of **1** with Re(CO)₅BF₄ or Mn₂(CO)₁₀, respectively (Fig. 5).

### 2.2. From (1-oxabuta-1,3-diene)tetracarbonyliron(0) complexes

In several examples, 1-oxabuta-1,3-diene complexes have been used as starting materials for the synthesis of 1-azabuta-1,3-diene complexes. In some cases, pre-formed (1-oxabuta-1,3-diene)tetracarbonyliron(0) complexes **43–45** have been reacted with a primary amine to yield the tricarbonyliron(0) complexes **1**, **46** and **47**
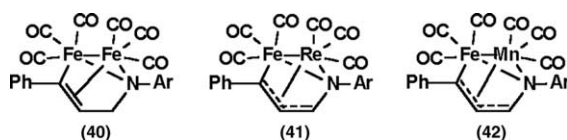


Fig. 5.

[3,29]. Here, the initial complexation of the tetracarbonyliron(0) moiety to the alkene directs primary amines to react at the uncoordinated carbonyl carbon of the 1-oxabuta-1,3-diene ligand and hence produce the 1-azabuta-1,3-diene complexes (**1**), (**46**) and (**47**) after loss of a carbonyl and co-ordination of the alkene (Scheme 9). This method also prevents the unwanted Michael additions of amines to the 1-oxabuta-1,3-diene and is particularly useful for the synthesis of complexes derived from ligands prone to polymerisation.

Alternatively, 1-azabuta-1,3-diene complexes may be synthesised by treatment of (1-oxabuta-1,3-diene)tetracarbonyliron(0) complex (**48**) with boron trifluoride followed by reaction of the resulting adduct **49** with a primary amine (Scheme 10) [30,31]. In these examples, the reaction proceeds via formation of allylic complex **50**, which is in equilibrium with $\eta^2$-(1-azabuta-1,3-diene)tetracarbonyliron(0) complex (**51**) where co-ordination to the iron moiety occurs through the alkene part of the 1-azabuta-1,3-diene and not the nitrogen lone pair. When the reaction mixture is warmed, CO loss occurs and formation of the $\eta^4$-complexes (**53**) is observed. This final step of the reaction has been demonstrated to proceed via the intermediacy of the 16-electron σ-*N*-imine complexes (**52**) [30–33].

Two examples of the crystal structures of the intermediate complexes of the type **50** formed during these conversions have been obtained [34,35]. They clearly show, as in Fig. 6, that in the solid phase the $\eta^3$-allyl form is the major tautomer.

In the solution phase, the equilibrium between the $\eta^3$-allyl and $\eta^2$-olefin forms of the complex is significantly more complicated and has been shown to be solvent- and structure-dependent [32]. In polar solvents the equilibrium shifts toward the $\eta^3$-allyl forms of complexes **50**. This factor has been attributed to the increased solvation of the open form in more polar solvents. The relationship between the ligand structure and the equilibrium position is more complex [33]. It was demonstrated that when the substituent at C-1 is bulky, the $\eta^3$-allyl complexes **50** also predominate. When branched alkyl substituents are at nitrogen, the $\eta^2$-complex (**51**) predominates. These findings may be explained in terms of the mutual repulsion of substituents. In the
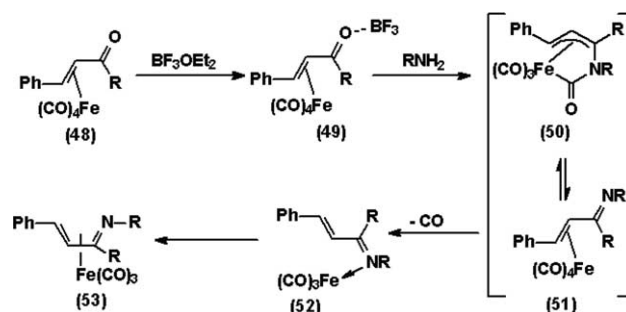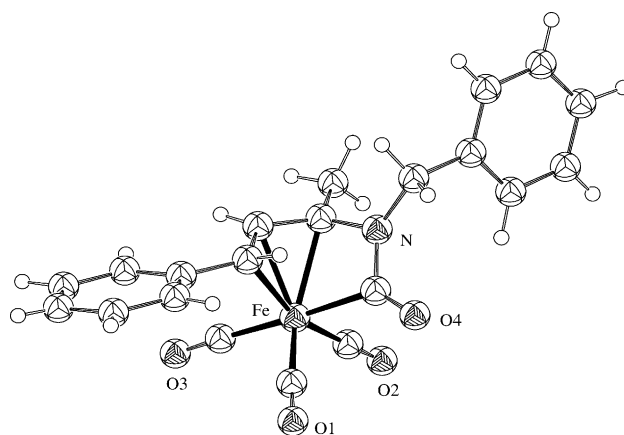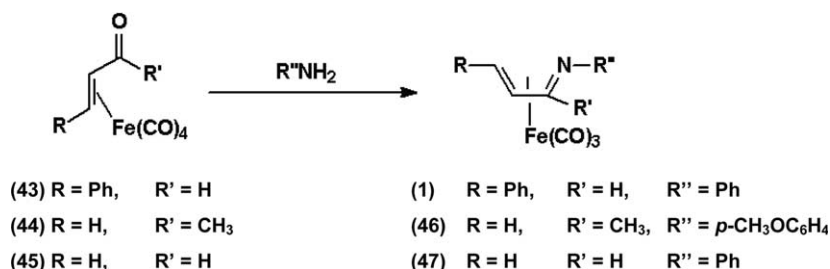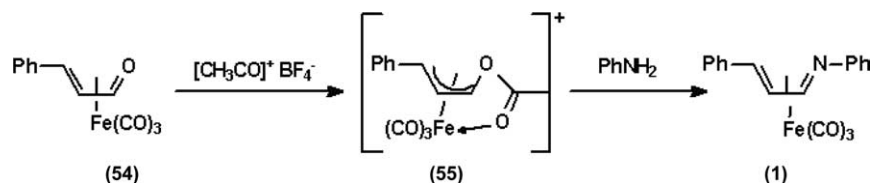


Scheme 10.



Fig. 6. Crystal structure of a complex of the type **50** [35].

$\eta^2$-olefin form there is a significantly increased interaction between the substituent at nitrogen, and the substituent at C-1. This interaction is significantly reduced when the complex adopts the $\eta^3$-allyl tautomer. For a branched substituent at nitrogen there is a significant interaction between the group at nitrogen and the oxygen of the bridging carbonyl group of the $\eta^3$-allyl form. Consequently, in this case the open $\eta^2$-olefin form of the complex tends to predominate.

It was also shown that the $\eta^2$-olefin form of the complex is more stable at higher temperature. Thermochemical measurements indeed confirm that conversion of the $\eta^2$-olefin form into the $\eta^3$-allyl form is an endothermic process and thereby rationalises this observation. Measurements also indicate that there is an increase in



| | | | | | | |
|---|---|---|---|---|---|---|
| (**43**) | R = Ph, | R' = H | | (**1**) | R = Ph, | R' = H, | R'' = Ph |
| (**44**) | R = H, | R' = CH₃ | | (**46**) | R = H, | R' = CH₃, | R'' = *p*-CH₃OC₆H₄ |
| (**45**) | R = H, | R' = H | | (**47**) | R = H | R' = H | R'' = Ph |

Scheme 9.

Scheme 11.

entropy on conversion to the $\eta^2$-olefin form of the complex, and indeed the equilibrium appears to be entropically controlled. This observation was explained in terms of the enhanced motion available to this complex compared to the closed and more rigid $\eta^3$-allyl form.

In other cases, (1-oxabuta-1,3-diene)tricarbonyliron(0) complex (**54**) has also been converted into its 1-azabuta-1,3-diene counterpart by reaction with acetylinium cation [(CH$_3$CO)$^+$] followed by treatment of the cationic intermediate $\eta^3$-allyl complex with a primary amine [36], leading to complex (**1**) (Scheme 11). This reaction has been shown to proceed via initial formation of the cationic allyl complex (**55**).

Functionalised (1-azabuta-1,3-diene)tricarbonyliron(0) complexes have been synthesised by aza-Wittig chemistry [37]. For example, treatment of tetracarbonyliron(0) complex (**56**) with *N*-phenyl triphenyl phosphorane leads to 1-azabuta-1,3-diene complex (**57**) upon warming (Scheme 12). Treatment of complex **57** with mild acid leads to an aldehyde substituted 1-azabuta-1,3-diene complex (**58**). Treatment of complex **58** with methylmagnesium iodide leads to an equi-molar mixture of diasteromeric complexes **59a** and **59b**, which were easily separated by column chromatography.
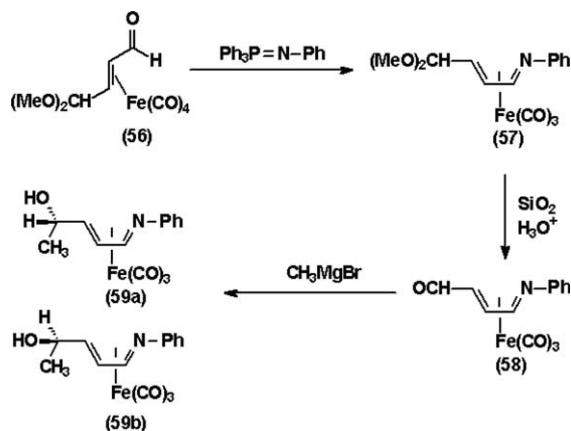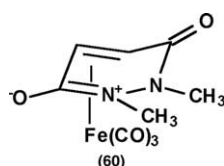


Scheme 12.



Fig. 7.

A slightly more unusual complex was prepared by reaction of Fe$_2$(CO)$_9$ with 1,2-dimethyl-1,2-dihydropyridazine-3,6-dione [38]. In the major reaction product the ligand was trapped in an unusual resonance form as tricarbonyliron(0) complex (**60**), as shown in Fig. 7. Similar complexes have been synthesised from 1-methyl-2-phenyl-1,2-dihydropyridazine-3,6-dione.

## 3. Structure

The structure of a (1-azabuta-1,3-diene)tricarbonyliron(0) complex was first determined for the parent system **1** derived from cinnamaldehyde and aniline (Fig. 8) [39,40]. Two distinct crystal forms were observed, a plate-like monoclinic form and a needle-like orthorhombic modification. In the former case, four molecular units are found in the unit cell, whereas in the latter there are six. The $\eta^4$-coordinated 1-azabuta-1,3-diene fragment is approximately planar to the tricarbonyliron(0) moiety in a way similar to that observed for the related buta-1,3-diene complex. The nitrogen iron bond distance indicates that the lone pair does not play a significant part in the bonding. The N to C-1 bond distance is 1.32 Å, which implies that the bond order is significantly greater than 1. The C-2 to C-3 bond distance is 1.36 Å [compared to 1.45 Å for (buta-1,3-diene)tricarbonyliron(0)] and is closer to that observed in (hexafluorobuta-1,3-diene)tricarbonyliron(0) (1.37 Å). In the preferred conformation, two carbonyl ligands are arranged underneath the coordinated C=C and C=N bonds of the 1-azabuta-1,3-diene, the third one thus points towards the space between the nitrogen atom and C-4. X-ray structural analysis of other derivatives shows a similar picture, with only little variation of structural parameters [11,26,41–44]. Also, a number of complexes in which one or two carbonyl ligands are
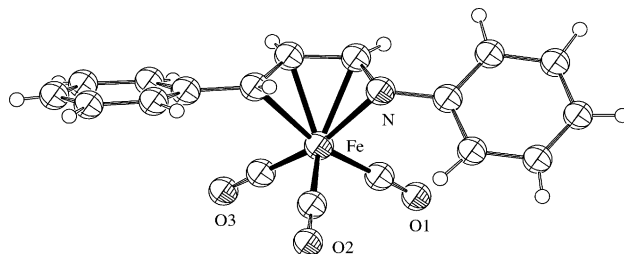


Fig. 8. Crystal structure of (PhCH=CHCH=NPh)Fe(CO)$_3$ (**1**) [40].

exchanged for phosphine or phosphite were structurally analysed and showed the same binding mode of the 1-azabuta-1,3-diene moiety [45].

The $^1H$ NMR spectrum (CDCl$_3$) of **1** contains doublets at ~3.25 (H-4) and ~5.64 ppm (H-3) ($J$ = 12 Hz) and a multiplet at 6.00–7.00 ppm (aromatics and H-2). The high field shift of the signals due to the H-3 (0–0.5 ppm) and H-4 (2.0–4.0 ppm) compared to the free ligand are typical of π-olefins [8,46] bound to the tricarbonyliron(0) moiety. The exceptional high field shift for proton (H-4) was attributed to the enhanced shielding experienced by the proton being located directly over the tricarbonyliron(0) moiety. Reduction in the coupling constant is attributed to the reduced dihedral angle of the ligand when it adopts the *cisoid* configuration associated with complexation.

The $^{13}C$ NMR spectrum shows the signals of the carbonyl ligands between 205 and 215 ppm. The coordinated carbon atoms of the azadiene typically appear in a range between 60 and 120 ppm, at lower chemical shifts than those of the corresponding free ligands [43,44]. Coordination to the iron centre reduces the double bond character of the 1-azabuta-1,3-diene, the chemical shifts therefore to approximate values typically found for aliphatic systems.

Infra-red spectra of these complexes show characteristic bands due to carbonyl ligands between 2070 and 1990 cm$^{-1}$. Signals due to the C=C and C=N are also present at 1475 and 1429 cm$^{-1}$ compared to 1621 and 1571 cm$^{-1}$ for the free 1-azabuta-1,3-diene ligand, respectively. This shift to lower wavenumbers was attributed to the reduction in bond order of the C=C and C=N bonds on coordination to the tricarbonyliron(0) moiety [3].

The fluxionality of the 1-azabuta-1,3-diene complexes (**1**) and its methoxy-substituted analogues has been studied by $^{13}C$ NMR in d$^8$-toluene [43,47]. It has been shown that the tricarbonyliron(0) moiety undergoes a temperature-dependent turnstile type rotation. For [1-(*p*-methoxyphenyl)-4-phenyl-1-azabuta-1,3-diene]tricarbonyliron(0), a single $^{13}C$ NMR signal is observed for the iron carbonyls at 209.9 ppm and at 338 K. This signal splits into three distinct signals at 261 K. The coalescence temperature for the iron carbonyl signals was shown to be 313 ± 10 K. From these data, the free energy of activation for the turnstile rotation of the tricarbonyliron(0) moiety was determined as 13.8 ± 0.5 kcal/mol.

Other complexes have also been studied and in general the coalescence temperature is in the range 308–338 K and the barrier for the rotation varies between 13.5 ± 5 and 14.7 ± 0.5 kcal/mol.

Another type of dynamic behaviour of (1-azabuta-1,3-diene)tricarbonyliron(0) complexes consists in migration of the tricarbonyliron moiety from one side of the 1-azabuta-1,3-diene ligand to the other one (Scheme 13). This effect was studied using the diastereomeric complexes **61a** and **61b**, which could be separated at low temperature (typically −30 to −45 °C) [11]. At temperatures above 0 °C, epimerisation took place, most likely via a 16-electron σ-bound imine complex **62**. The activation energy for this process was determined to be 22.4 ± 1 kcal/mol.

## 4. Reactivity

### 4.1. Ligand exchange reactions

#### 4.1.1. Azabuta-1,3-diene ligands

In a similar way to the 1-oxabuta-1,3-diene complexes [48], (1-azabuta-1,3-diene)tricarbonyliron(0) complexes can be utilised as a source of the tricarbonyliron(0) moiety during the synthesis of (homo-1,3-diene)tricarbonyliron(0) complexes. For example, warming a mixture of 1-azabuta-1,3-diene complex (**1**) with cyclohexa-1,3-diene (**63**) leads to the formation of (cyclohexa-1,3-diene)tricarbonyliron(0) (**64**) in good yield (Scheme 14) [49].

The reaction has been shown to proceed via initial formation of the 16-electron σ-*N* complex **65**. Co-ordination of cyclohexa-1,3-diene (**63**) to compound (**65**) leads to complex **66** which upon loss of the 1-azabuta-1,3-diene leads to the formation of complex **64** (Scheme 15).

The exchange procedures have also been shown to proceed under catalytic conditions where only a small quantity of the 1-azabuta-1,3-diene is added to the reaction mixture of Fe$_2$(CO)$_9$ and the diene [27,44,50]. In these cases, the transfer is not only thought to proceed via the (1-azabuta-1,3-diene)tricarbonyliron(0) complexes but also to involve the diiron cluster **40**. Evidence for the latter has been obtained. When complex **40** is warmed with cyclohexa-1,3-diene (**63**), formation of (cyclohexa-1,3-diene)tricarbonyliron(0) (**64**) is observed (Scheme 16).
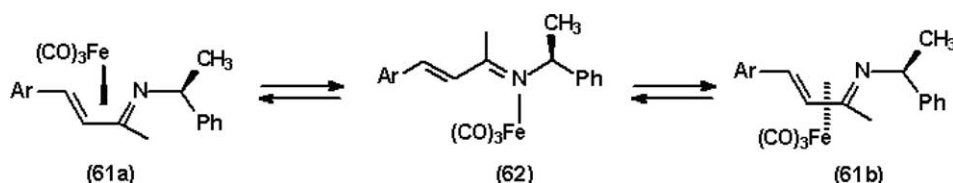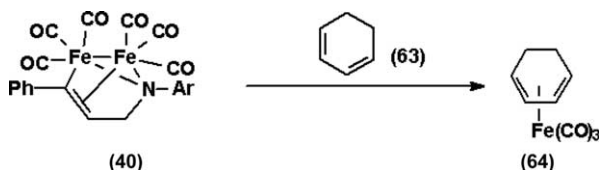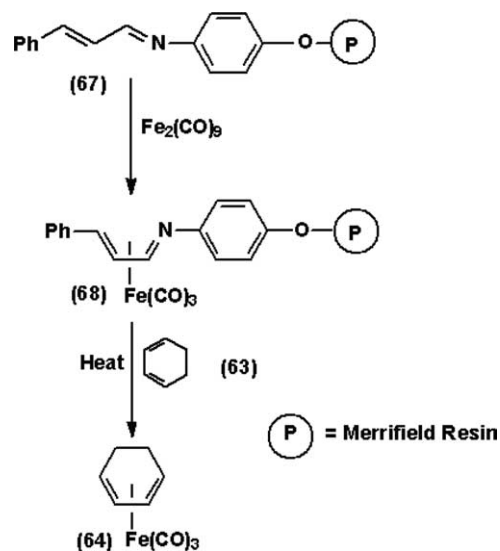


Scheme 13.
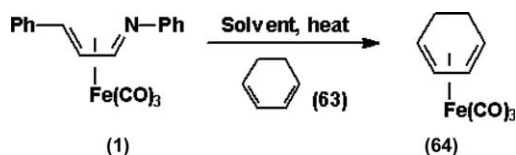
Scheme 14.
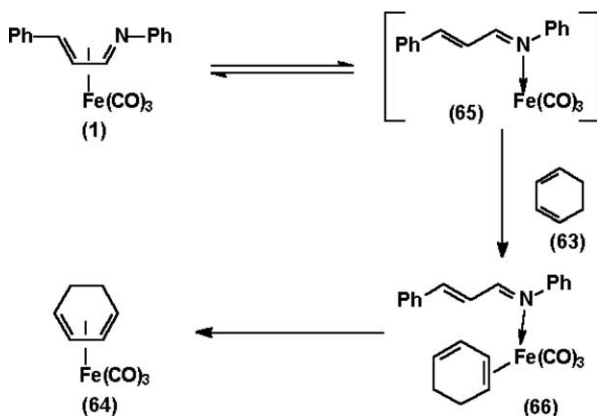


Scheme 15.



Scheme 16.



Scheme 17.

In many cases, the exchange reaction proceeds efficiently under thermal or sono-chemical conditions and has been routinely used for the synthesis of tricarbonyliron(0) complexes of functionalised cyclohexa-1,3-dienes [51].

Further development of these exchange reactions has led to a polymer supported 1-azabuta-1,3-diene (67), which can be converted into the corresponding (1-azabuta-1,3-diene)tricarbonyliron(0) complex (68) after reaction with $Fe_2(CO)_9$ under sono-chemical conditions (Scheme 17) [39]. This polymer-supported complex readily transferred the $Fe(CO)_3$ moiety to cyclohexa-1,3-diene (63) under thermal conditions. The authors reported that this approach allowed the production of a reusable source of the transfer agent to be developed and stated that the polymer supported ligand could be reused up to six times without loss of activity.

Asymmetric ligand exchange reactions have also been reported. For example, reaction of a chiral 1-azabuta-1,3-diene complex with a prochiral 1,3-diene leads to facially selective transfer of the tricarbonyliron(0) moiety

and formation of an enantiomerically enriched (1,3-diene)tricarbonyliron(0) complex. Complexes derived from simple cinnamaldehyde-based ligands (e.g., 20) and more elaborate ferrocene 69 [52], *bi*-naphthyl 70 [52], camphor 71 [53], amino acid [54] or aminosugar [55]-based systems, amongst others, have been used for these reactions (Fig. 9). Transfer of the tricarbonyliron(0) to 1-methoxycyclohexa-1,3-diene has been achieved in up to 62% enantiomeric excess. In a more recent paper, the enantiomeric excesses of the complexes produced by this route have been increased considerably when the exchange reaction is performed under photochemical conditions using $Fe(CO)_5$ as the source of the tricarbonyliron(0) moiety [56].

Ligand exchange reactions from 1-azabuta-1,3-diene complexes bearing co-ligands other than carbonyls have also been observed [11]. For example, reaction of *R* or *S* (1-(1-phenylethyl)-4-phenyl-1-azabuta-1,3-diene)dicarbonyl triphenylphosphineiron(0) (28) with 1-methoxycyclohexa-1,3-diene (72) leads to the formation of optically active complexes 73 (Scheme 18). No information regarding the efficiency of this exchange, however, was provided.

The photochemical substitution of 1-azabuta-1,3-diene ligands has also been reported [57]. For example, photolysis of an *n*-hexane solution of complex 74 [R = $CH(CH_3)_2$, R′ = Ph] at 293 K in the presence of a fivefold excess of ligand 75 [R = *p*-$CH_3$-$C_6H_4$, R′ = Ph] leads to a mixture of the original complex 74 and new complex 76 (Fig. 10). The fact that more starting complex was observed in the product mixture was attributed to the fact that ligand 77 [R = $CH(CH_3)_2$, R′ = Ph] was more basic than ligand 75 [R = *p*-$CH_3$–$C_6H_4$, R′ = Ph].

When the reaction was performed in a methane matrix at 10 K, the 16-electron complexes 78 and 79

Fig. 9.



Scheme 18.



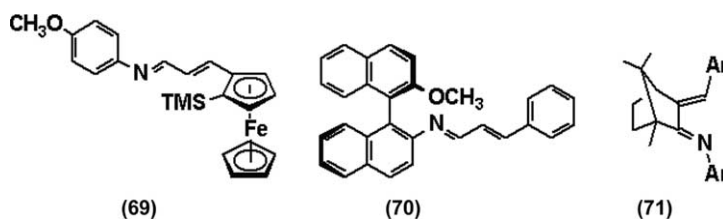(74)  R = CH(CH$_3$)$_2$     (77)  R = CH(CH$_3$)$_2$
(76)  R = p-CH$_3$-C$_6$H$_4$   (75)  R = p-CH$_3$-C$_6$H$_4$
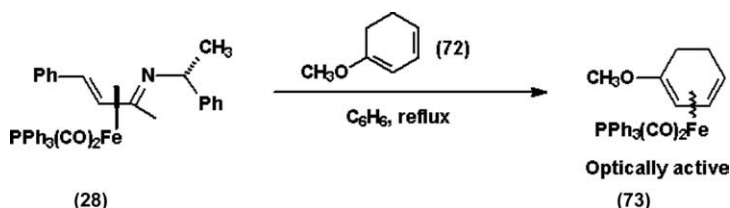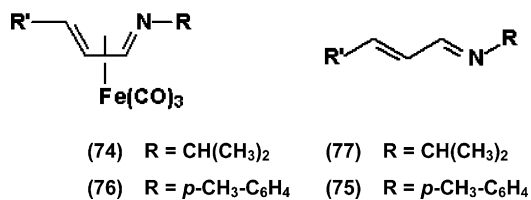
Fig. 10.

are observed (Scheme 19) [57]. When the mixture was allowed to warm to 293 K, the original complexes **74** and **76** were reformed. Evidence for the formation of the 16-electron complexes was obtained from solid-state infrared spectra.

### 4.1.2. Substitution of carbonyl ligands

The first report of ligand substitution of carbonyl ligand appeared in 1967 [3]. It was shown that reaction of complex **1** with triphenyl phosphine leads to the formation of the mono-substituted complex **80** (Scheme 20). Attempts to repeat this reaction on complex **2** derived from crotonaldehyde and n-butylamine leads to the formation of (PPh$_3$)$_2$Fe(CO)$_3$ **81** as the sole reaction product. This difference in the behaviour of complexes **1** and **2** was attributed to the more weakly bound 1-azabuta-1,3-diene ligand in the latter case and the generally higher reactivity of complex **2**.



(74)  R = CH(CH$_3$)$_2$          (78)  R = CH(CH$_3$)$_2$
(76)  R = p-CH$_3$-C$_6$H$_4$       (79)  R = p-CH$_3$-C$_6$H$_4$
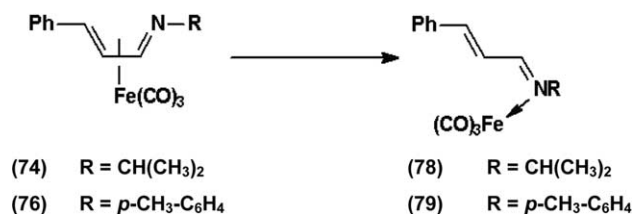
Scheme 19.

The reaction of 1-azabuta-1,3-diene complexes with group-V ligands has been the subject of kinetic and mechanistic studies and shown to proceed via either associative or dissociative mechanism [58]. The dissociative path for the complex **1** proceeds via 16 electron σ-N complex **82** which in the presence of an external ligand readily converts to complex **83**, and further to complex **84** after loss of a carbonyl ligand and coordination of the 1-azabuta-1,3-diene or otherwise Fe(CO)$_3$L$_2$ (**85**) and the free 1-azabuta-1,3-diene (**3**) after reaction of a second external ligand. An alternative associative reaction path leads directly to complex **83** which then converts to either complexes **84** or **85** by loss of a carbonyl ligand or by addition of a second external ligand, respectively.

The mechanism of the substitution reaction appears to vary with both the nature of the 1-azabuta-1,3-diene and group V ligands involved. For example, for a weakly bound 1-azabuta-1,3-diene ligand, the more basic phosphines lead to the formation of *bis* phosphine tricarbonyliron(0) (**85**), whereas the more strongly bound 1-azabuta-1,3-diene tends to follow the carbonyl substitution reaction pathway and lead to the formation of phosphine dicarbonyliron(0) type 1-azabuta-1,3-diene complexes (**84**) (Scheme 21).

Kinetic studies have shown that the mechanism of these substitution reactions depends upon the nature of the group V ligand [59–61]. Kinetics of the substitution reactions has been determined for PPh$_3$ and P$^n$Bu$_3$. Kinetic data for reaction of AsPh$_3$or SbPh$_3$ with complex **1** could not be satisfactorily obtained owing to an incomplete reaction. The observation of the incomplete reaction was attributed to the reversibility of the substitution reaction, where carbon monoxide (generated from the initial substitution reaction) readily replaced the group V ligands on the substituted complexes.
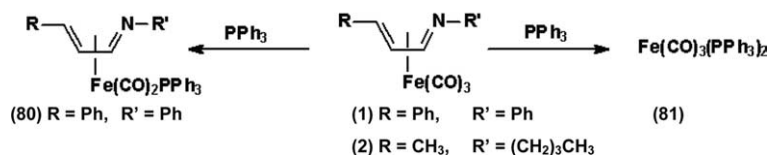
Scheme 20.
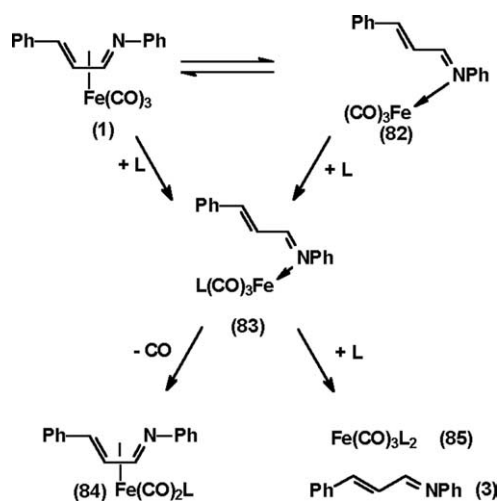


Scheme 21.



Scheme 22.

Further evidence for this observation was obtained when the isolated complexes (containing AsPh$_3$ or SbPh$_3$) were stirred under an atmosphere of carbon monoxide; in these cases the reactions led to the formation of complex **1**. This reaction is thought to again proceed via formation of an σ-*N* complex and the ease of displacement of the group V ligand is related to the relative basicity of the group V ligand (PPh$_3$ ≫ AsPh$_3$ > SbPh$_3$).
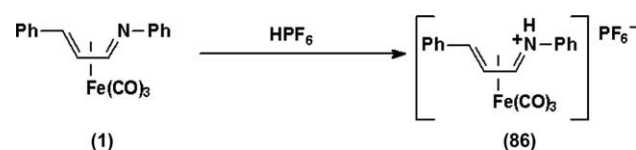
### 4.2. Reactions involving the co-ordinated 1-azabuta-1,3-diene

#### 4.2.1. Reaction with electrophiles

The reactions of the co-ordinated 1-azabuta-1,3-diene have been reported by several workers. The first report concerned protonation reactions [8]. It was shown that reaction of (1,4-diphenyl-1-azabuta-1,3-diene)tricarbonyliron(0) (**1**) with hexafluorophosphoric acid leads to protonation at nitrogen and formation of the cationic complex **86** (Scheme 22). Complex **86** was shown to be moderately stable and could be isolated. In the presence of some solvents (e.g. water, ethanol and chloroform), **86** was readily deprotonated to generate the original complex **1**. Evidence for the synthesis of **86** was obtained from infrared and $^1$H NMR spectroscopy.

#### 4.2.2. Reaction with nucleophiles

Treatment of the complexes with nucleophiles leads to the formation of several reaction products. For com-

plex **13**, reaction with methyl lithium leads to attack at a co-ordinated carbonyl group and formation of an anionic iron acyl complex **87** [4,5]. After insertion of the acyl fragment into the co-ordinated 1-azabuta-1,3-diene, and the anionic azaallyl intermediate **88** is formed. Its protonation, followed by ring closure and loss of water leads to pyrrole **89** as the sole reaction product (Scheme 23). The extremely mild reaction conditions required for this reaction (−78 °C, 6 h) compared to those for classical pyrrole synthesis from a 1,4-diketone and a primary amine via the Paal Knorr route (120 °C, 3–10 h) indicate that the ironcarbonyl moiety is likely to be involved in the ring closure step. This reaction has been demonstrated for a range of complexes containing aryl and alkyl substituents at C-4 and nitrogen and either H or CH$_3$ at C-2.

Alternatively, the reaction appears to proceed via attack at the imine carbon and leads to the formation of an allylic amine **90**. For example, treatment of complex **1** with methyl-lithium followed by a proton source leads to the formation of allylic amine **90** [4]. The same allylic amine **90** was also formed when the free 1-azabuta-1,3-
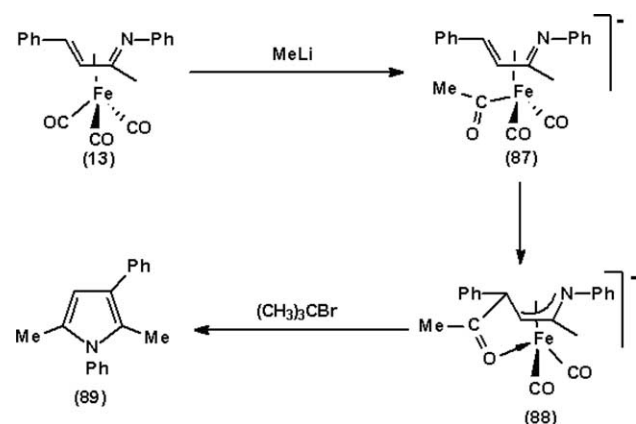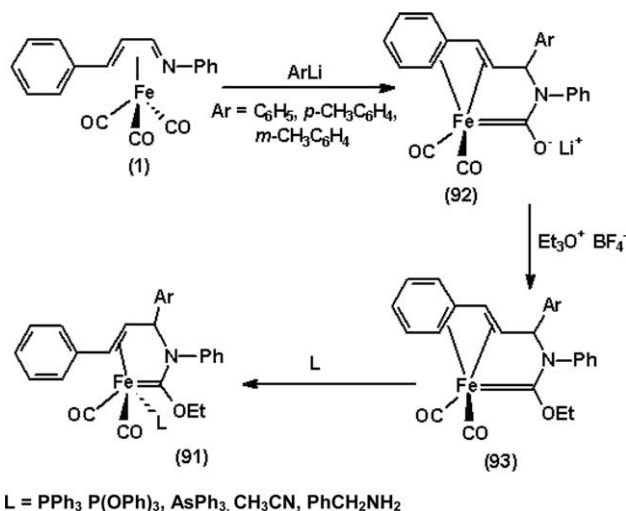


Scheme 23.

diene (3) was treated with methyl-lithium under identical conditions (Scheme 24).

When complex 1 is treated with an aryl-lithium reagent followed by triethyl oxonium tetrafluoroborate, carbene complexes 91 are formed [62]. In this reaction, initial nucleophilic addition occurs at C-2 of the co-ordinated 1-azabuta-1,3-diene, followed by attack of nitrogen at an iron carbonyl ligand leading to complex 92. Addition of triethyloxonium tetrafluoroborate leads to the styryl carbonyl complex 93 in which the alkene and part of the benzene ring is co-ordinated to a dicarbonyliron(0) carbene moiety. Treatment of 93 with a group V ligand leads to the detachment of the aromatic ring from the co-ordination sphere and formation of the $\eta^2$-alkene-carbene complex 93 (Scheme 25).

Depending on the substituents on the 1-azabuta-1,3-diene and the general reaction conditions, different reaction patterns are observed [63]. The reaction of 1-azabuta-1,3-diene complex (94) with ArLi leads to arylation at one of the carbonyl ligands to produce the anionic acyl complex 95 in which the negative charge is delocalised over the acyl group and the iron atom. When this complex is treated with triethyl oxonium tetrafluoroborate, a one-electron oxidation process is reported to take place to convert the Fe(0) complex 95 into a Fe(I) species 96 whose structure was determined by X-ray diffraction. In an atmosphere of CO, the reaction takes a different course to produce the zwitterionic complex 98 under uptake of CO to form 97 and subsequent N-alkylation (Scheme 26). Also the structure of 97 was confirmed by X-ray crystallography.

The reactivity of 1-azabuta-1,3-diene complexes (99) with lithium aluminiumhydride has also received attention. It has been shown that the reaction leads to the formation of saturated amines 100 in good yield (Scheme 27) [64,65]. No reaction is observed for sodium borohydride under identical conditions or even when the reaction mixture is exposed to prolonged periods of reflux. Reaction of the free 1-azabuta-1,3-dienes with either lithium aluminiumhydride or sodium borohydride leads to the formation of allylic amines only. There is no evidence for the fully saturated amine even after prolonged reflux [64].

Deuteration experiments indicate that three deuterium atoms are incorporated in the product and result



L = PPh₃ P(OPh)₃, AsPh₃, CH₃CN, PhCH₂NH₂

Scheme 25.

in the formation of 1,2,3-trideutero amines (101) and (102) (Fig. 11) [65].

Under microwave irradiation, however, sodium borohydride may be used to affect this reduction [66]. It is of note, however, that the temperatures of these microwave reactions could not be recorded, and it is therefore uncertain whether the activation of sodium borohydride is a result of the rapid heating or whether there is any specific "microwave effect". Under the same conditions, use of sodium borodeuteride in place of LiAlD₄ leads to the identical isotope pattern as observed in the thermal reaction.

Studies of the reaction between hydride transfer reagents and homo-1,3-diene complexes using super hydride® or LiAlH₄ have revealed that the reaction proceeds via formation of an iron formyl intermediate [67]. The suggestion of a similar intermediate was also proposed for the reduction of the 1-azabuta-1,3-diene complexes.

More recently, the reaction between 1-azabuta-1,3-diene complexes and lithiated amines has been studied and this leads to either an enamine complex or an organic formamide [68]. It has been demonstrated that the path of the reaction is dependent upon the substituent at C-2 of the co-ordinated ligand. In the cases where the substituent is hydrogen, the reaction proceeds via nucleophilic attack at an iron carbonyl ligand and formation of formamides 103 after addition of a



Scheme 24.

Scheme 26.



Scheme 27.



Scheme 29.



Fig. 11.
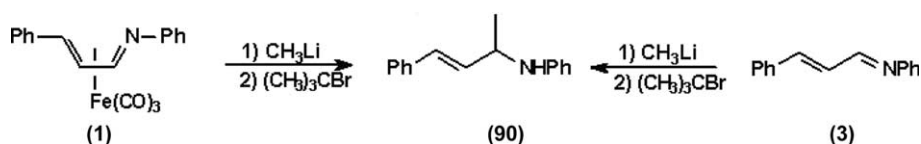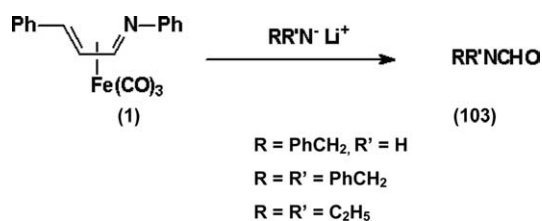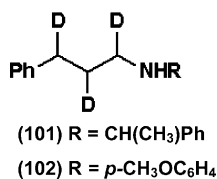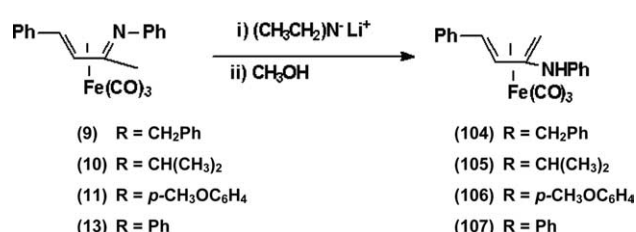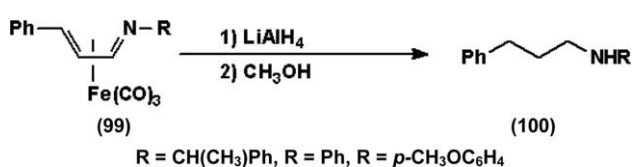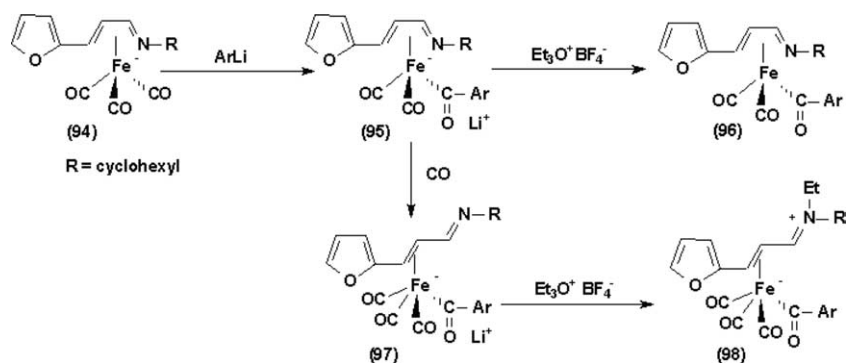


Scheme 28.

proton source (Scheme 28). This reaction was proposed to proceed via nucleophilic attack at a co-ordinated carbonyl ligand followed by protonation and decomplexation.

When the substituent at C-2 is a methyl group as in **9–11** and **13**, reaction with a lithium amide leads to deprotonation and formation of secondary enamine complexes **104–107** after addition of a proton source (Scheme 29) [6,68].

The formation of enamine complex **107** may be described in terms of initial deprotonation of the methyl group at C-2 of complex **13** by the lithium diethylamide to yield the carbanionic complex **108** [6]. Rearrangement of **108** into the $\eta^3$-azaallyl complex **109**, in which the negative charge is centred on iron, facilitates rotation of the bond between C-2 and C-3. This leads to the formation of complex **110** and nitrogen, the centred anionic homodiene complex **111**, after recoordination of the $\pi$-bond between C-3 and C-4. Protonation of **111** at nitrogen, upon addition of methanol, leads to the formation of the novel enamine complex **106** (Scheme 30).

When the reaction is quenched using an alkyl halide instead of a proton source, formation of tertiary (enamine)tricarbonyliron(0) complexes **112** results [69]. The crystal structure of two examples of complexes of this type have been obtained [70]. All attempts to synthesise these complexes by treatment of the secondary enamine complexes **107** with alkylating agents did not produce the desired compounds **112** but converted the enamine complexes back into the starting azadiene complex **13**. However, the secondary enamide complexes **107** can be deprotonated with butyl-lithium and then alkylated to give the tertiary enamine complexes **112** (Scheme 31).

When complexes **113** containing an ethyl group at C-2 are treated with lithium diethylamide, an enamine complex is produced as a reaction product. Of the

Scheme 30.

Scheme 31.
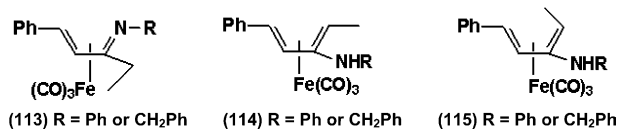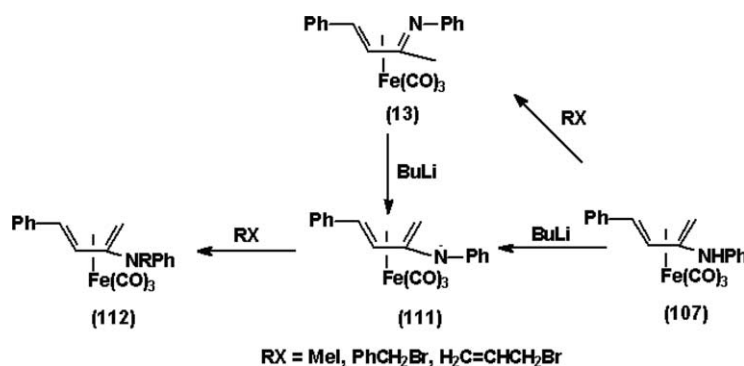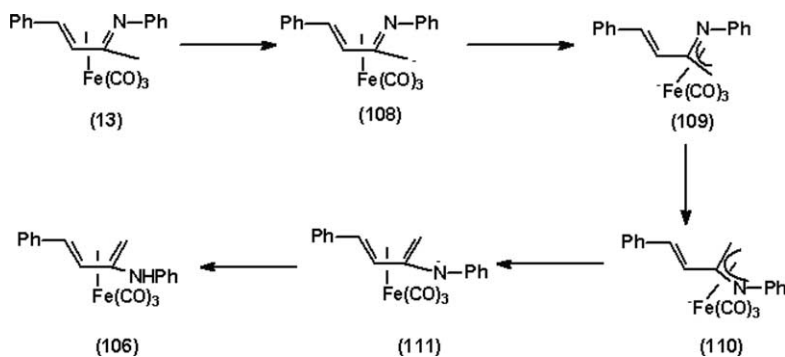
RX = MeI, PhCH$_2$Br, H$_2$C=CHCH$_2$Br

Fig. 12.

two possible products **114** and **115**, only the complex **115** in which the methyl group at C-1 is in the *endo* position is observed (Fig. 12) [7]. Confirmation of the reaction products structure was obtained from $^1$H NMR and NOE difference spectroscopy.

This observation has been rationalised in terms of a conformationally constrained ethyl group at C-2 that is oriented away from the substituent at nitrogen [7]. Evidence for such an arrangement in **113** was obtained on the basis of NOE difference spectroscopy. The resulting stereochemistry of the product **115** is assumed to arise from similar conformational constraints in the $\eta^3$-co-ordinated 1-azabuta-1,3-diene in
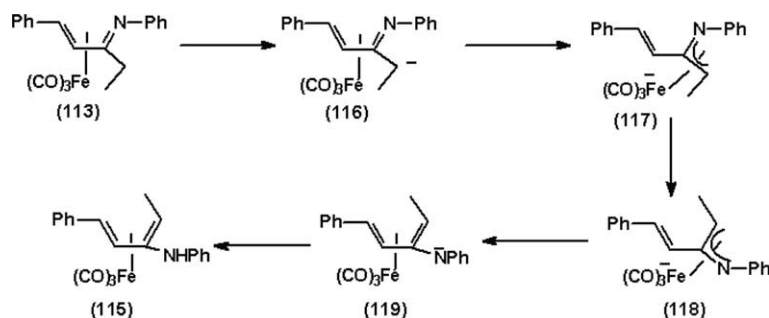
Scheme 32.

the intermediate $\eta^3$-azaallyl complexes **117** and **118** (Scheme 32).

## 5. Conclusions

In conclusion, it can be seen that structural aspects of the (1-aza-1,3-diene)tricarbonyliron(0) complexes are well understood and the chemistry of these systems has developed significantly over the last 35 years. Initial reports of simple protonation reactions have been extended, and the reaction of these complexes with nucleophiles has illustrated their utility in organic and organometallic synthesis. Similarly, extensive work on the use of these systems as transfer reagent for the tricarbonyliron(0) moiety has led not only to the development of useful protocols for the synthesis of 1,3-diene complexes but has additionally allowed asymmetric complexation reactions to be developed. An additional advantage of the (1-aza-1,3-diene)tricarbonyliron(0) systems is the ease at which these complexes may be synthesised from simple and readily available starting materials in high yield, to provide what are usually stable and easily manipulated precursors to a range of important synthetic targets and simple isotopically labelled substrates.

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