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Preparation, fluxionality and some reactions of ring-linked $[Fe_2\{\eta,\eta-C_5H_4-A-B-C_5H_4\}(CO)_{4-n}(CNMe)_n]$ complexes

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Abstract

$[Fe_2\{\eta,\eta-C_5H_4-A-B-C_5H_4\}(CO)_2(\mu-CO)_2]$ reacts with CNMe in refluxing xylene when A-B = *R,S*-CH(NMe$_2$)CH(NMe$_2$) or CH$_2$C(O) to give $[Fe_2\{\eta,\eta-C_5H_4-A-B-C_5H_4\}(CO)_{4-n}(CNMe)_n]$ ($n = 1$ or 2). This thermal reaction does not take place when A-B = *R,R/S,S*-CH(NMe$_2$)CH(NMe$_2$), CH$_2$CH(NMe$_2$), CHC(NMe$_2$), CH$_2$CH(OH) or CH$_2$CH$_2$, but photolysis allows the preparation of $[Fe_2\{\eta,\eta-C_5H_4-A-B-C_5H_4\}(CO)_{4-n}(CNMe)_n]$ (n = 1–3), and $[Fe_2\{\eta,\eta-C_5H_4CH_2CH(OH)C_5H_4\}(CO)_3(CNMe)]$ may be prepared by the LiAlH$_4$-reduction of $[Fe_2\{\eta,\eta-C_5H_4CH_2C(O)C_5H_4\}(CO)_3(CNMe)]$. All the complexes react with MeI, EtI or MeOSO$_2$CF$_3$ to give derivatives containing one or two μ-CNMe$_2^+$ ligands. ^{1}H NMR studies show that all the neutral complexes are fluxional, with processes taking place within the C$_5$H$_4$-A-B-C$_5$H$_4$ ligands comparable to those observed in the tetracarbonyl precursors as well as CO/CNMe site exchange. This last is more restricted than in the $[Fe_2(\eta-C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ counterparts, so that two non-interconverting $[Fe_2\{\eta,\eta-C_5H_4-A-B-C_5H_4\}(CO)_2(CNMe)_2]$ species are possible, and have been separated in most instances; one has the structure $[Fe_2\{\eta,\eta-C_5H_4-A-B-C_5H_4\}(CO)(CNMe)(\mu-CO)(\mu-CNMe)]$ and the other is $[Fe_2\{\eta,\eta-C_5H_4-A-B-C_5H_4\}(CO)_2(\mu-CNMe)_2]$, which is in equilibrium with $[Fe_2\{\eta,\eta-C_5H_4-A-B-C_5H_4\}(CNMe)_2(\mu-CO)_2]$ in solution. Their formation provides unequivocal evidence for the validity of the Cotton–Adams rules on fluxionality in $[Fe_2(\eta-C_5H_5)_2(CO)_4]$ derivatives. The structure of *R,S*-$[Fe_2\{\eta,\eta-C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu-CNMe)_2]$ has been determined by an X-ray diffraction study.

Keywords: Iron; Carbonyl; Cyclopentadienyl; Fluxionality; Isocyanide

1. Introduction

cis–trans isomerism and ligand site-exchange in $[Fe_2(\eta-C_5H_5)_2(L)_2(\mu-L)_2]$ complexes (L = CO or organoisocyanide) appear to obey the Cotton–Adams Rules [1] with some modification [2]. These rules suggest that two non-interconverting isomers are possible for complexes of the general type *cis*-$[Fe_2(\eta-C_5H_5)_2(L)_2(L')_2]$ [3]. This is illustrated in Fig. 1. The four ligands, a–d may be divided into two pairs, a/b and c/d. Both members of each pair are either terminally coordinated or bridging in all species accessible by the Cotton–Adams mechanism; there is not random scrambling of the ligands over the four available sites. As we have prepared a series of ring-linked $[Fe_2\{\eta,\eta-C_5H_4-A-B-C_5H_4\}(CO)_2(\mu-CO)_2]$ which are constrained to a *cis* configuration (Fig. 2) [4,5], it seemed an ideal opportunity to prepare such compounds to see if the predicted isomers can be obtained. We report here on the reactions of various $[Fe_2\{\eta,\eta-C_5H_4-A-B-C_5H_4\}(CO)_2(\mu-CO)_2]$ (A-B = *R,S*-CH(NMe$_2$)CH(NMe$_2$), *R,R/S,S*-CH(NMe$_2$)CH(NMe$_2$), CH$_2$C(O), CH$_2$CH(NMe$_2$), CHC(NMe$_2$), or CH$_2$CH(OH) with CNMe, which give $[Fe_2\{\eta,\eta-C_5H_4-A-B-C_5H_4\}(CO)_{4-n}(CNMe)_n]$ (n = 1, 2 or 3), and the successful separation of many $[Fe_2\{\eta,\eta-C_5H_4-A-B-C_5H_4\}(CO)_2(\mu-CNMe)_2]$ from $[Fe_2\{\eta,\eta-C_5H_4-A-B-C_5H_4\}(CO)(CNMe)(\mu-CO)(\mu-CNMe)]$. We have also confirmed a previous observation that the CO-substitution reactivities of $[Fe_2\{\eta,\eta-C_5H_4-A-B-C_5H_4\}(CO)_2(\mu-CO)_2]$ are a function of the ring-linking group A-B [6] for CNMe as the incoming ligand, as they are for P(III) compounds. Also reported are the reactions of $[Fe_2(\eta,\eta-C_5H_4-A-$

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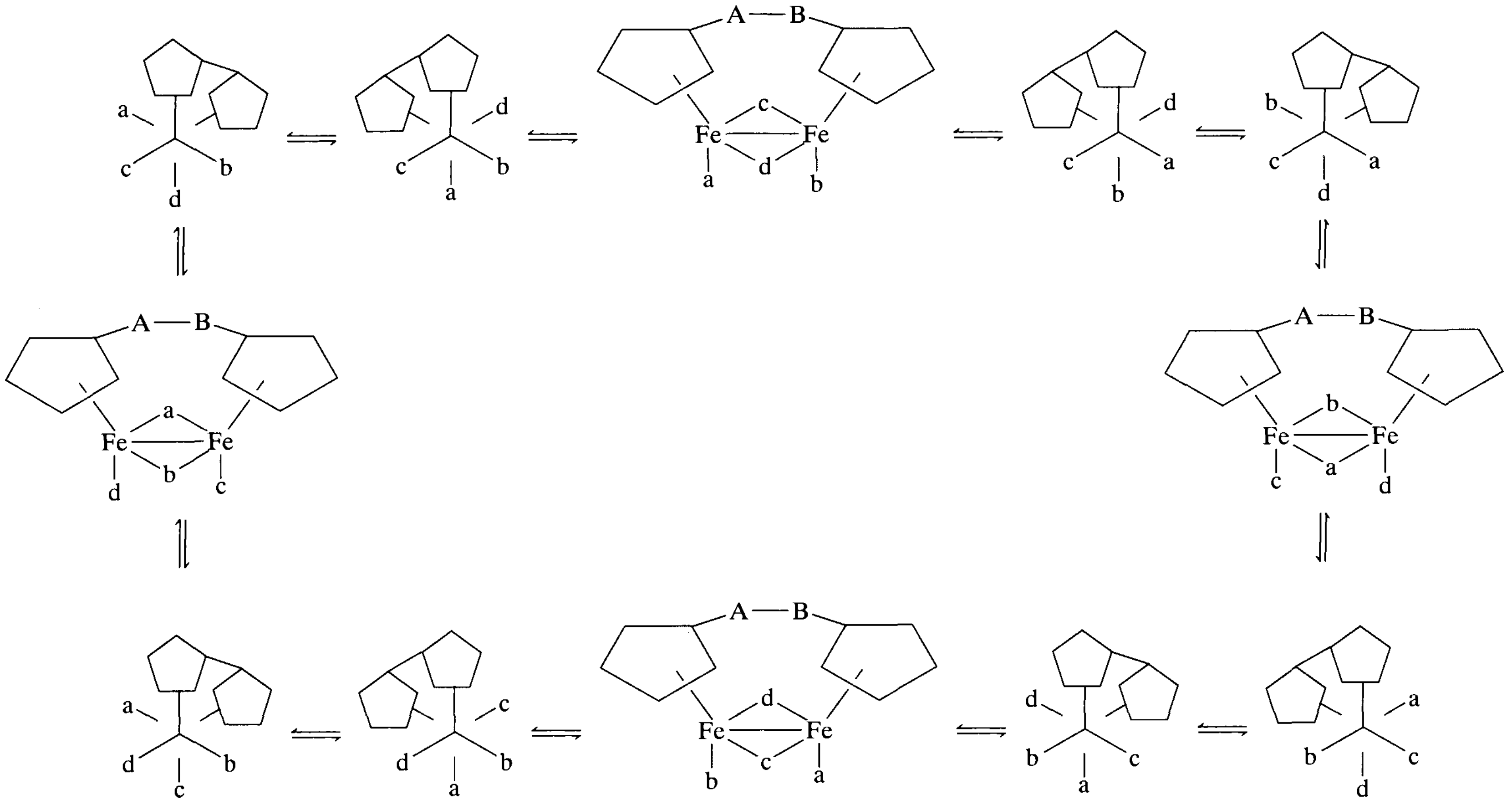

Fig. 1. The Cotton–Adams mechanism for the ligand exchange processes in a [$Fe_2\{\eta,\eta\text{-}C_5H_4\text{-}A\text{-}B\text{-}C_5H_4\}(a)(b)(c)(d)$] system. $n = 1$ a = CNMe, b = c = d = CO; $n = 2(\mu\text{-}\mu/t,t$ species) a = b = CNMe, c = d = CO; $n = 2(\mu\text{-}t$ species) a = c = CNMe, b = d = CO.

B-$C_5H_4\}(CO)_{4-n}(CNMe)_n]$ with alkylating agents and some limited attempts to modify the A-B group by conventional organic chemistry (cf. Ref. [5]).

Whilst this manuscript was in preparation, various $[Fe_2\{\eta,\eta\text{-}C_5H_4SiMe_2C_5H_4\}(CO)_{4-n}(CNR)_n]$ ($n = 1$ or 2, and R = alkyl) were reported [7].

2. Experimental section

Previously published methods were used to prepare $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$ {A-B = *R*,*S*-CH(NMe_2)CH(NMe_2) [8], *R*,*R*/*S*,*S*-CH(NMe_2)CH(NMe_2) [8], $CH_2C(O)$ [5], and CHC(NMe_2) [5], CH_2-CH(NMe_2) [5] and CH_2CH_2 [5]} and CNMe [9]. Other chemicals were purchased.

All reactions were carried out under nitrogen in solvents that had been dried and deoxygenated by refluxing over calcium hydride. They were monitored by IR spectroscopy.

2.1. The reactions of $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$ with CNMe

A solution of $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2C(O)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$ (0.6 g) and CNMe (0.6 cm^3) in xylene (50 cm^3) was refluxed for 2 h. The cooled solution was filtered and chromatographed on alumina. Elution with dichloromethane and recrystallization from a toluene/pentane mixture gave $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2C(O)C_5H_4\}(CO)_3(CNMe)]$ as brown crystals in 50% yield. A second band was eluted with acetone. It gave a purple oil which was identified as $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2C(O)C_5H_4\}(CO)_2(CNMe)_2]$ (yield 30%). This was dissolved in the minimum of toluene and the solution was kept at −15°C for 2 months during which purple crystals of $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2C(O)C_5H_4\}(CO)_2(\mu\text{-}CNMe)_2]$ separated. They were filtered off and allowed to dry (yield 10%). The mother liquor was then chromatographed on an alumina column. Slow elution with acetone/toluene gave some $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2C(O)C_5H_4\}(CO)_2(\mu\text{-}CNMe)_2]$ followed by $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2C(O)C_5H_4\}(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe)]$; the latter was isolated by removal of the solvent at reduced pressure and recrystallized from toluene/pentane mixtures (yield 10%).

A solution of *R*,*S*-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$ (1.0 g) and CNMe (1.2 cm^3) in xylene (150 cm^3) was refluxed for 30 min. The solvent was removed at reduced pressure, and the residue chromatographed on alumina. Elution with benzene/dichloromethane and recrystallization from a toluene/pentane mixture gave *R*,*S*-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_3(CNMe)]$ as purple crystals in 65% yield. Elution with dichloromethane-acetone and recrystallization from hot diethylether gave *R*,*S*-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CNMe)_2]$ as a red powder in 20% yield. A repetition of this experiment gave *R*,*S*-$Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_3(CNMe)]$ as before, but the second band to be eluted was a mixture of *R*,*S*-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CNMe)_2]$ and *R*,*S*-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe)]$. These were separated by chromatography using a longer column, and each was recrystallized from toluene/pentane mixtures.

There was no reaction between $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_4]$ and CNMe under the above conditions when A-B = *R*,*R*/*S*,*S*-CH(NMe_2)CH(NMe_2), $CH_2CH(NMe_2)$, CHC(NMe_2) and CH_2CH_2. However for these complexes substitution was effected when the reaction mixture was irradiated with a 400 W UV lamp in an Applied Photophysics photochemical reactor for 10 h to give $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_{4-n}(CNMe)_n]$.

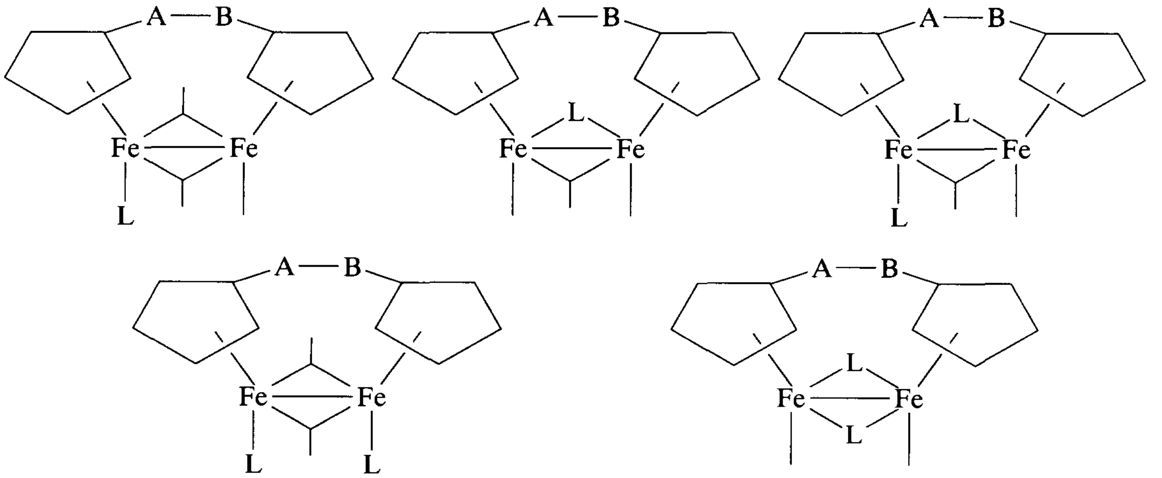

Fig. 2. The structures of the various isomers of $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_{4-n}(CNMe)_n]$ ($n = 1$ and 2). CO groups have been omitted for the sake of clarity, and L = CNMe.

(n = 1–3). These were separated and purified as described above.

2.2. *The reaction of [$Fe_2\{\eta,\eta$-$C_5H_4CH_2C(O)C_5H_4\}$-$(CO)_3(CNMe)$] with $LiAlH_4$*

[$Fe_2\{\eta,\eta$-$C_5H_4CH_2C(O)C_5H_4\}(CO)_3(CNMe)$] (0.5 g) was dissolved in diethyl ether (70 cm^3) and a five-fold excess of $LiAlH_4$ was added. An immediate reaction took place. The solution was filtered and a few drops of water were added to the filtrate, which was then evaporated to dryness. The residue was recrystallized from dichloromethane-hexane to give red crystals of [$Fe_2\{\eta,\eta$-$C_5H_4CH_2CH(OH)C_5H_4\}(CO)_3(CNMe)$] in 60% yield.

2.3. *The reactions of [$Fe_2\{\eta,\eta$-C_5H_4-A-B-$C_5H_4\}$-$(CO)_{4-n}(CNMe)_n$] (n = 1, 2 or 3) with MeI, EtI or $MeOSO_2CF_3$*

The reactions were carried out at room temperature as described in Ref. [10] for the similar reactions of [$Fe_2(\eta - C_5H_5)_2(CO)_{4-n}(CNMe)_n$]. The reactions including $MeOSO_2CF_3$ were virtually instantaneous, but those of MeI took 1–3 h and that of EtI 16 h. The salts, listed in Table 1, were obtained in yields of 70–85% except for *R,S*-[$Fe_2\{\eta,\eta$-$C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu$-$CO)\{\mu$-$CN(Me)R\}$]I (R = Me or Et), where the reactions were stopped before completion and yields were ca. 30% or less.

Elemental analyses (Tables 1 and 2) were carried out by the Analytical Laboratory of University College, Dublin. IR spectra (Tables 3 and 4) were run on Perkin Elmer 1710 and 1720 FTIR spectrometers, and ^1H NMR spectra (Tables 5 and 6) on a JEOL JNM-GX270 spectrometer.

2.4. *Structure of R,S-[$Fe_2\{\eta,\eta$-$C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu$-$CNMe)_2$]*

Crystal data are summarised in Table 7. The structure was solved by direct methods, SHELX86 [11], and refined by full matrix least squares, SHELX76 [12]. Data were collected on an Hilger Y290 diffractometer and were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions with fixed thermal parameters. The iron atoms and the carbon, oxygen and nitrogen atoms of the carbonyl and methyl isocyanide groups were refined anisotropically and the other non-hydrogen atoms were refined isotropically. All calculations were carried out on a VAX 6610 computer. The atomic scattering factors for non-hydrogen atoms, and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature [13–15]. A perspective drawing of the molecule [16] with the atom labelling scheme is given in Fig. 3. The atom parameters are given in Table 8, and selected bond lengths and bond angles in Table 9. A complete list of bond lengths and bond angles, and tables of thermal param-

Table 1
Analyses for the [$Fe_2\{\eta,\eta$-C_5H_4-A-B-$C_5H_4\}(CO)(L)(\mu$-$CO)_{2-n}(\mu$-$CNMe_2)_n$][Y]$_n$ salts

L	n	Y^-	Analyses [a,b]			
			%C	%H	%N	%S or %I
A-B = *R/S*-$CH(NMe_2)CH(NMe_3)^+Y^-$						
CO	1	$[BPh_4]^-.MeCN$	72.9(73.2)	6.2(6.3)	5.9(5.7)	
CNMe	1	$[SO_3CF_3]^-$	39.2(39.5)	4.2(4.3)	6.6(7.0)	
CO	2	$[SO_3CF_3]^-$	37.9(38.1)	4.2(4.2)	6.6(6.8)	
A-B = *R,R/S,S*-$CH(NMe_2)CH(NMe_2)$						
CO	1	I^-	41.3(42.6)	4.3(4.3)	6.2(6.8)	I = 20.7(20.5)
CO	1	I^-	42.9(43.5)	4.7(5.0)	6.3(6.6)	I = 19.9(20.0)
A-B = *R,R/S,S*-$CH(NMe_2)CH(NMe_3)^+Y^-$						
CO	1	$[SO_3CF_3^-]^-.H_2O$	36.4(36.8)	3.9(4.3)	4.9(5.1)	S = 8.1(7.8)
CO	1	$I^-.1/2C_6H_6$	41.5(41.4)	5.1(4.4)	5.1(5.0)	
CO	1	$[BPh_4]^-$	73.9(74.3)	5.9(6.2)	3.2(3.7)	
CNMe	1	$[SO_3CF_3]^-$	39.1(39.5)	4.3(4.3)	6.7(7.1)	
CO	2	$SO_3CF_3.2H_2O$	32.5(32.9)	3.7(4.0)	5.2(5.5)	S = 9.5(9.4)
A-B = $CH_2CH(OH)$						
CO	1	$[SO_3CF_3]^-.1/2CH_2Cl_2$	36.9(37.0)	2.8(2.9)	1.9(2.2)	
A-B = $CH_2C(O)$						
CO	1	$[SO_3CF_3]^-.2H_2O$	37.9(37.6)	2.8(3.3)	2.3(2.3)	S = 5.1(5.3)
CO	1	I^-	39.3(39.3)	3.0(2.9)	2.5(2.5)	I = 22.2(23.1)
CNMe	1	$[SO_3CF_3]^-$	40.5(41.0)	3.4(3.3)	4.5(4.8)	S = 5.7(5.5)
CNMe	1	I^-	40.5(40.6)	3.5(3.4)	4.7(5.0)	I = 22.4(22.6)
CO	2	$[SO_3CF_3]^-.2H_2O$	35.2(35.0)	3.0(3.4)	3.9(3.7)	S = 8.3(8.5)

[a] All compounds decomposed on heating at 180–200°C.
[b] Calculated values in parentheses.

eters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

The CO substitution reactions of $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$ with PR_3, $P(OR)_3$ and $Ph_2P(CH_2)_nPPh_2$ ($n = 1$, 2 or 3) are much slower than the corresponding reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)_2]$ and are greatly affected by the nature of A-B [6]. Similar patterns of behaviour have been found for the reactions with CNMe. Thus it is possible to replace CO by CNMe using thermal reactions in refluxing xylene when A-B = *R*,*S*-$CH(NMe_2)CH(NMe_2)$ or $CH_2C(O)$ to give $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_{4-n}(CNMe)_n]$ but not when A-B = *R*,*R*/*S*,*S*-$CH(NMe_2)CH(NMe_2)$, $CH_2CH(NMe_2)$, or $CHC(NMe_2)$. For these UV irradiation using a 400 W mercury lamp is necessary to bring about substitution to give the complexes where $n = 1$, 2 or 3, but when A-B = CH_2CH_2 decomposition occur and no such products are obtained. In all of these reactions the ring-linking group A-B was unaffected, unlike those of *R*,*S*-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$ with $Ph_2P(CH_2)_nPPh_2$ when $n = 2$ or 3 which also gave $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2C(O)C_5H_4\}\{Ph_2P(CH_2)_nPPh_2\}(\mu\text{-}CO_2)]$ [6]. However, when A-B = $CHC(NMe_2)$ product separation by chromatography resulted in hydrolysis of the enamine to ketone and the isolation of complexes where A-B = $CH_2C(O)$.

Two non-interconverting isomers of the $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_2(CNMe)_2]$ complexes are formed. Their separation is difficult and tedious, and could not be achieved for A-B = $CH_2CH(NMe_2)$. However pure samples of both were obtained when A-B = *R*,*S* and *R*,*R*/*S*,*S*-$CH(NMe_2)CH(NMe_2)$, and $CH_2C(O)$. In the solid state one has a $Fe_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe)$ moiety and the other $Fe_2(CO)_2(\mu\text{-}CNMe)_2$.

The $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_{4-n}(CNMe)_n]$ complexes are red solids. They are stable in air at room temperature, but are susceptible to oxidation in solution.

3.1. Infrared spectra

Of the many absorption bands in the IR spectra, only those due to $\nu(CO)$ and $\nu(CN)$ stretching vibrations yield structural information. Their frequencies and relative intensities are summarised in Table 3. The assignments are straightforward and made by comparison with data for related systems [2,20]. When A-B = $CH_2C(O)$ the spectra contain an absorption band of medium intensity at ca. 1685 cm^{-1} owing to the ketone $\nu(CO)$ vibration.

Table 2
Melting points and analyses of $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_{4-n}(CNMe)_n]$ complexes describe in the text

n	M.p. (°C) [a]	Analyses [b]			
		%C	%H	%N	%Fe
A-B = *R*,*S*-$CH(NMe_2)CH(NMe_2)$					
1	137- 40	52.4(52.6)	5.5(5.2)	8.6(8.8)	
2 [c]	188–192	53.5(53.7)	5.8(5.7)	11.1(11.4)	
2 [d]	186–189	53.7(53.7)	5.9(5.7)	10.9(11.4)	
A-B = *R*,*R*/*S*,*S*-$CH(NMe_2)CH(NMe_2)$					
1	dec. 155	52.8(52.6)	5.2(5.3)	8.7(8.7)	
1 [e]	89- 92	53.7(53.6)	5.6(5.5)	8.1(8.5)	
2 [c]	dec. 170	52.6(53.7)	6.2(5.7)	9.4(11.4)	
2 [d]	dec. 170	53.9(53.7)	6.2(5.7)	10.1(11.4)	
3	dec. 165	53.9(54.6)	6.3(6.1)	10.1(13.9)	
A-B = $CH_2C(O)$					
1 [f]	219–221	52.3(52.5)	3.9(3.9)	3.6(3.2)	25.5(25.7)
2 [c]	184–186	51.8(51.4)	3.9(3.8)	6.5(6.7)	26.1(26.6)
2 [d]	dec. 150	51.8(51.4)	3.9(3.8)	6.5(6.7)	27.0(26.6)
A-B = $CH_2CH(NMe_2)$					
1	144–147	52.7(52.3)	4.9(4.6)	6.1(6.4)	
2 [g]	dec. 165	60.4(59.9)	6.6(5.7)	8.4(7.8)	
A-B = $CH_2CH(OH)$					
1	200–202	49.5(49.9)	3.7(3.7)	3.3(3.4)	27.6(27.4)

[a] Melting points determined in sealed tubes; dec. denotes decomposition.
[b] Calculated values in parentheses.
[c] $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_2(\mu\text{-}CNMe)_2]$ isomer.
[d] $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe)]$ isomer.
[e] CNEt complex.
[f] 1/3 C_6H_{14} of crystallization.
[g] Unseparated mixture of isomers. With toluene of crystallization.

The spectra show that in the solid state the $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe)]$ structure is found when A-B = *R*,*S*-$CH(NMe_2)CH(NMe_2)$, *R*,*R*/*S*,*S*-$CH(NMe_2)CH(NMe_2)$, and $CH_2CH(OH)$ {cf. *cis*-$[Fe_2\{\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNCH_2Ph)]$ [17]}, and the $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)(CNMe)(\mu\text{-}CO)_2]$ structure when X = $CH_2C(O)$ {cf. *cis*-$[Fe_2\{\eta\text{-}C_5H_5)_2(CO)(CNBu\text{-}t)(\mu\text{-}CO)_2]$ [18]}. One of the two isomers of the $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_2(CNMe)_2]$ complexes has the $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_2(\mu\text{-}CNMe)_2]$ structure similar to that of *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$ [19] whilst the other is $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe)]$ like *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNPr^i)(\mu\text{-}CO)(\mu\text{-}CN^iPr)]$ [2]. The only species we have isolated containing three CNMe ligands was found to be *R*,*R*/*S*,*S*-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)(CNMe)(\mu\text{-}CNMe)_2]$ both in the solid state and in solution. The structure of some of the isomers are illustrated in Fig. 2.

Table 3
Infrared spectra of $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_{4-n}(CNMe)_n]$ complexes between 1600 and 2200 cm^{-1}

n	Solvent	Absorption Bands [a]			
		^tCNMe	^tCO	μ-CO	μ-CNMe
A-B = *R*,*S*-$CH(NMe_2)CH(NMe_2)$					
1	CH_2Cl_2	2151(2.9)	1985(10) 1947(5.6)	1781(2.4) 1742(7.4)	1722(sh)
1	CS_2	– [b]	1988(10) 1950(4.0)	1756(3.5) 1793(1.7)	1726(2.5)
1	pentane	2138(0.9)	1997(10) 1959(4.5)	1807(3.7) 1796(2.1) 1771(3.3)	1737(3.2) 1727(3.7)
1	KBr		1977(10) 1964(10) 1932(8.7)		1708(8.6)
2 [c]	CH_2Cl_2		1976(10) 1939(2.2)		1703(6.0)
2 [c]	CS_2	– [b]	1981(10) 1946(3.1)		1712(6.9)
2 [c]	pentane		1990(10) 1954(2.3)		1718(4.3)
2 [c]	KBr		1972(10) 1929(5.2)		1703(7.6)
2 [d]	$CHCl_3$	2148(8.0)	1950(8.2)	1755(4.5)	1693(10)
2 [d]	hexane	2133(6.1)	1952(9.4) 1946(10)	1788(7.6)	1709(8.2)
2 [d]	KBr	2143(6.9)	1942(10)	1768(5.7)	1691(6.3)
A-B = *R*,*R*/*S*,*S*-$CH(NMe_2)CH(NMe_2)$					
1	$CHCl_3$	2155(2.3)	1999(10) 1959(4.1)	1770(3.9)	1733(4.4)
1	KBr		1986(10) 1950(3.3)	1774(4.0)	1707(4.5)
2 [c]	$CHCl_3$	2150(0.6)	1984(10) 1954(5.2)	1770(sh)	1693(9.3)
2 [c]	hexane		1990(10) 1955(2.6)		1716(3.4)
2 [c]	KBr		1981(10) 1940(3.2)		1693(7.1)
2 [d]	$CHCl_3$	2150(9.2)	1952(10)	1755(4.4, br)	1693(10)
2 [d]	KBr	2147(7.2)	1940(10)	1764(6.2)	1690(7.9)
3	$CHCl_3$	2146(7.7)	1946(7.7)		1662(10)
3	hexane	2133(5.5)	1947(10)		1664(8.5)
3	KBr	2141(6.8)	1947(10)		1685(10)
$CH_2C(O)$					
1	xylene	2153(3.3)	1995(7.2) 1957(7.0)	1798(1.5) 1770(10)	1741(1.8)
1	KBr	2161(8.2)	1993(10) 1957(4.2) 1942(1.1)	1752(10)	
2 [c]	CH_3CN	2155(2)	1982(10) 1945(2.4)	1733(5.2)	1718(6.7)
2 [c]	$CHCl_3$	2152(1.8)	1996(10) 1959(2.7)	1722(sh)	1708(7.4)
2 [c]	toluene		1987(10) 1952(1.5)	–	1757(0.5)
2 [c]	CS_2	– [b]	1989(10) 1954(2.2)	–	1723(6.0)
2 [c]	KBr		1985(10) 1935(4.5)		1709(10)
2 [d]	$CHCl_3$	2157(3.8)	1997(10) 1962(4.9)	1775(1.9)	1708(8.5)
s [d]	toluene	2150(2.7)	1987(10) 1948(6.7)	1780(2.4)	1723(8.8)
2 [d]	KBr	2154(5.8)	1935(7.8)	1763(8.1)	1707(10)
$CH_2CH(NMe_2)$					
1	$CHCl_3$	2154(5.9)	1992(8.1) 1957(7.5)	1776(4.0)	1730(10)
1	Hexane	2139(0.5)	1996(10) 1957(7.3)	1799(4.5) 1789(2.3,sh) 1770(3.0)	1732(5.1)
2 [c]	$CHCl_3$		1988(10) 1952(4.1)		1695(9.3)
$CH_2CH(OH)$					
1	$CHCl_3$	2157(6.1)	1996(9.6) 1959(7.5)	1781(3.3) 1734(10)	1713(7.8)
2	CH_2Cl_2	2154(4.2)	1988(9.6) 1951(6.9)	1784(2.7) 1745(10)	1730(sh)

[a] Peak positions (cm^{-1}) with relative peak heights in parentheses. For assignment see text.

[b] Obscured by solvent absorption.

[c] $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_2(\mu\text{-}CNMe)_2]$ isomer.

[d] $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe)]$ isomer.

In solution $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_{4-n}(CNMe)_n]$ complexes in which $n = 1$ or 2 (but not 3) isomerise to solvent-dependent equilibrium mixtures of isomers, although constrained to the *cis* configuration. It is clear from IR and NMR spectra that, the *t*-CNMe isomers are favoured by increasing solvent polarity as has been found for their $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ counterparts (cf. Ref. [20]) and by varying A-B along the series *R*,*S* and *R*,*R*/*S*,*S*-CH(NMe$_2$)CH(NMe$_2$) < CH$_2$C(O) < CH$_2$CH(OH). The IR spectra of $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe)]$ are independent of the solvent, suggesting that these complexes do not isomerise to other species, but $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_2(\mu\text{-}CNMe)_2]$ may be in equilibrium with $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CNMe)_2(\mu\text{-}CO)_2]$. Further details of these equilibria and the fluxional processes involved in them will be discussed below.

3.2. ^{1}H NMR spectra and fluxionality

The ^{1}H NMR spectra are summarised in Tables 5 and 6. They confirm that the groups A-B remain unchanged throughout the various reactions (except for the possible conversion of NMe$_2$ into NMe$_3^+$), adopt the same conformations as in their tetracarbonyl precursors, and undergo the same fluxional processes [5] with comparable $\Delta G^{\ddagger}_{Tc}$ values, viz. 10.6 kcal mol^{-1} for the restricted rotation about the linking C–C bond when A-B = *R*,*S*-CH(NMe$_2$)CH(NMe$_2$), and 8.9 kcal mol^{-1} for the rotation–inversion of the NMe$_2$ groups when A-B = *R*,*S* and *R*,*R*/*S*,*S*-CH(NMe$_2$)CH(NMe$_2$). These processes will not be discussed further except when they affect the remainder of the molecule.

The presence of the CNMe ligands can modify the ^{1}H NMR resonances of the linking A-B group and the C$_5$H$_4$ ligands. Those of the latter are often too complicated to be assigned in detail and are of little use, but the former can be important. For example, the two CH$_2$ protons in $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2C(O)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$ are identical on the NMR timescale and always give rise to a singlet resonance [5], but in $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2C(O)C_5H_4\}(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe)]$ they are different, and two doublets are usually observed. The same is true for the CHCH protons in *R*,*R*/*S*,*S*-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe)]$, *R*,*R*/*S*,*S*-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)(CNMe)(\mu\text{-}CO)_2]$ and *R*,*S*-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)(CNMe)(\mu\text{-}CO)_2]$ even when restricted rotation about the linking C–C bond is fast for this last species. Conversely the linking group A-B may modify the molecular symmetry so that the two *μ* and two *t* sites of the Fe$_2$(L)$_2$(*μ*-L)$_2$ are distinguishable, as can be seen by inspection of Fig. 1. Thus when A-B = *R*,*R*/*S*,*S*-CH(NMe$_2$)CH(NMe$_2$) the two *μ* sites are indistinguishable and so are the two *t* sites, but the molecule does not possess a plane of symmetry; when A-B = *R*,*S*-CH(NMe$_2$)CH(NMe$_2$) the two *μ* sites are always different but the two *t* sites only become so when the partial rotation about the linking C–C bond slows (cf. Ref. [5]); when A-B = CH$_2$C(O) the two *t* sites are always different but the two *μ* sites are equivalent even at low temperatures (cf. Ref. [5]); and when A-B =

Table 4
IR spectra of the $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)(L)(\mu\text{-}CO)_{2-n}(\mu\text{-}CNMe_2)_n[Y]_n$ salts between 1550 and 220 cm^{-1} [a]

L	*n*	Y	Absorption bands				
			$\nu(\mu\text{-}C{=}NMe_2)$	$\nu(\mu\text{-}CO)$	$\nu(CO)$	$\nu(CO)$	$\nu(CNMe)$
X = *R*,*S*-CH(NMe$_2$)CH(NMe$_2$)							
CO [c]	1	I	1608(m)	1826(s)	1996(sh)	2012(vs)	
CO [b,c]	1	I	1603(m)	1823(s)	1980(sh)	2001(vs)	
X = *R*,*R*/*S*,*S*-CH(NMe$_2$)CH(NMe$_3$)$^+$[SO$_3$CF$_3$]$^-$							
CO	1	SO$_3$CF$_3$.2H$_2$O	1605(2.5)	1848(2.2)	2008(2)	2028(10)	
CO [d]	2	SO$_3$CF$_3$.2H$_2$O	1621(6)		2045(2.1)	2064(10)	
X = CH$_2$C(O)							
CO	1	SO$_3$CF$_3$.2H$_2$O	1604(3.9)	1851(2.3)	2001(2)	2030(10)	
CO	1	I	1604(4.0)	1850(2.3)	2001(2)	2029(10)	
CNM [e]	1	SO$_3$CF$_3$	1594(2.4)	1822(4.8)	1994(10)		2179(8.2)
CNM [e]	1	I	1599(6.3)	1820(5.6)	1992(10)		2179(7.7)
CO [d]	2	SO$_3$CF$_3$.2H$_2$O	1623(9.3)			2061(10)	
X = CH$_2$CH(OH)							
CO	1	SO$_3$CF$_3$.1/2CH$_2$Cl$_2$	1603(1.1)	1834(2.1)	1990 (1.5)	2022 (10)	

[a] Peak positions (cm^{-1}) with relative peak heights in parentheses. m = medium, sh = shoulder, s = strong, and vs = very strong. Spectra run in dichloromethane solution unless it is stated otherwise. For assignment see text.

[b] *μ*-CN(Me)Et ligand.

[c] Spectrum run in KBr pressed discs.

[d] Spectrum run in acetonitrile solution.

Table 5
^1H NMR spectra of the $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_{4-n}(CNMe)_n]$ complexes described in the text

n	Isomer [b]	Solvent [c]	T (K)	Resonances [a]				
				C_5H_4 [d]	CHCH, CH_2CH or CH_2	^tCNMe	μ-CNMe	NMe_2
A-B = R,S-CH(NMe$_2$)CH(NMe$_2$)								
1 [e]	μ	CD_2Cl_2/CS_2	273	5.32(2) 5.08(2) 5.00(4)	μ_b 2.99 μ_a 2.88		μ_b 3.63 μ_a 3.61	2.20, 2.19 (12, br)
1 [e]	t	CD_2Cl_2/CS_2	273	5.17(1) 5.12(1) 4.91(2) 4.86(1) 4.82(1) 4.79(1) 4.75(1)	2.93(1, d) 2.95(1, d) (J_{HH} = 2.8)	2.98(3)		ditto
2	μ-μ	CD_2Cl_2/CS_2	298	5.38(2) 5.24(2) 5.02(2) 4.98(2)	2.89		3.57(3) 3.60(3)	2.17(12)
	μ-μ	CD_2Cl_2/CS_2	193	5.0-5.6 (br)	2.68(d) 2.97(d) ($J_{(HH)}$ = 2)		3.57(3) 3.60(3)	2.16(12, br)
2 [f]	μ-t	$CDCl_3$	298	4.8–5.4(8; 10 resonances)	μ_b-t 3.02 μ_a-t 2.86(d) 2.91(d) ($J_{(HH)}$ = 2)	μ_b-t 2.96 μ_a-t 2.95	μ_b-t 3.74 μ_a-t 3.71	μ_b-t 2.20 μ_a-t 2.18
A-B = $R,R/S,S$-CH(NMe$_2$)CH(NMe$_2$)								
1		$CD_3C_6D_5$	353	4.88(4) 4.61(2) 4.43(2)	2.72(2, br)	2.2(3, br)	3.5(3, br)	1.83(12, br)
1 [g]	μ	$CD_3C_6D_5$	293	4.83(8) 4.65(1) 4.62(1) 4.58(1) 4.51(1) 4.44(2) 4.31(2)	2.68(2)	2.00(3)		1.80(6) 1.82(6)
1 [g]	t		293	ditto	2.54(1, d) 2.48(1, d) ($J_{(HH)}$ = 11.6)		3.54(3)	1.72(6) 1.73(6)
2	μ-t	$CDCl_3$	293	5.28(4) 5.19(3) 5.11(1) 4.81(1) 4.79(1) 4.74(2) 4.65(1) 4.61(1) 4.55(1) 4.50(1)	2.87(d) 2.62(d) ($J_{(HH)}$ = 11.1) 2.86(d) 2.63(d) ($J_{(HH)}$ = 11.1)	2.97(1.5) 2.98(1.5)	3.71(3)	1.93(12)
3		$CDCl_3$	293	5.40(1) 5.37(1) 5.22(2) 5.84(1) 4.74(10) 4.61(1) 4.45(1)	2.72(1, d) 2.71(1, d) ($J_{(HH)}$ = 11.5)	2.94(3)	3.67(6)	1.92(12)
A-B = CH$_2$C(O)								
1		$CD_3C_6D_5$	373	5.08(2) 4.83(2) 4.70(2) 4.63(2)	2.38(2)	2.60(3, br)		
1 [h]	μ	CD_2Cl_2	243	5.58(1) 5.57(3) 5.49(1) 5.03(1) 4.97(1)	2.97(d, 1) 2.92(d, 1) ($J_{(HH)}$ = 13)		3.71(3)	
1 [h]	t_a	CD_2Cl_2	243	5.34(4) 5.11(2) 4.87(2)	3.03(2)	2.83(3)		
1 [h]	t_b	CD_2Cl_2	243	5.34(4) 5.23(2) 4.93(2)	3.04(2)	2.84(3)		
2	μ-t	$CD_3C_6D_5$	373	5.4–4.4(br)	2.41	2.15(br)	3.66(br)	
2 [i]	μ-t	$CD_3C_6D_5$	293	μ-t_b 5.35 4.88 4.79 4.65 μ-t_a 5.40 5.00 4.94 4.84 4.70	μ-t_b 2.30 μ-t_a 2.29	μ-t_b 1.96 μ-t_a 1.94	μ-t_b 3.66 μ-t_a 3.63	
2	μ-μ	$CD_3C_6D_5$	293	5.03(2) 4.90(2) 4.80(2) 4.59(2)	2.20(2)		3.45(6)	
2 [j]	μ-μ	CD_3CN	293	5.65(2) 5.49(2) 5.41(2) 4.96(2)	2.85(2)		3.63(6)	
2 [j]	t-t	CD_3CN	293	5.16(2) 5.14(2) 4.91(2) 4.93(2)	2.67(2)	2.98(3) 2.99(3)		
A-B = CH$_2$CH(OH)								
1 [k]	μ&t	$CDCl_3$	298	4.6–5.6(8, 16 resonances)	4.1–4.3(1) 2.0–2.5(2)	2.998, 3.004 (3)	3.70, 3.72(3)	
A-B = CH$_2$CH(NMe$_2$)								
1	μ&t	$CDCl_3$	298	4.6–5.6(8, 18 resonances)	2.8–3.1(1) 2.1–2.4(1) 1.8–2.05(partly hidden)	2.99, 3.00(3)	3.704, 3.707 (3)	μ2.01, t2.02(6)

[a] Chemical shifts given as ppm downfield from Me_4Si as an internal standard. Resonances are singlets unless it is stated otherwise. d = doublet, m = multiplet, and br = broad. Integrations are given in parentheses. Coupling constants J are quoted in Hz..

[b] μ, t, μ-μ, t-t, and μ-t indicate isomers which respectively contain one μ-CNMe, one ^{t}CNMe, two μ-CNMe, two ^{t}CNMe, and one μ-CNMe/one ^{t}CNMe ligands. Subscript a indicates the major form of that isomer (e.g. μ_a) and subscript b the minor form (eg. t_b)

[c] CD_2Cl_2/CS_2 solvent ratio = ca. 1/1.

[d] All C_5H_4 resonances are multiplets. In some instances not all resonances can be identified or attributed due to the presence of isomers and CD_2Cl_2 resonances.

[e] $t:\mu_b:\mu_a$ ratio = 38:25:37.

[f] μ_a-$t:\mu_b$-t ratio = 65:35.

[g] $t:\mu$ ratio = ca. 17:18 so that C_5H_4 resonances cannot be attributed.

[h] $t_b:t_a:\mu$ ratio = 22:36:42.

[i] $\mu/t_b:\mu/t_a$ ratio = 40:60.

[j] t, $t:\mu$, μ ratio = 25:75.

[k] Two μ (ratio ca. 1:1) and two t (ratio 1:1) isomers present. $\Sigma t:\Sigma\mu$ = 63:37. Detailed assignment of complex multiplets due to C_5H_4 and CH_2CH protons is not possible.

$CH_2CH(OH)$ or $CH_2CH(NMe_2)$ all four sites are different. Therefore there may be more than one μ-CNMe or *t*-CNMe isomer of the $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-}A\text{-}B\text{-}C_5H_4\}(CO)_3CNMe]$ complexes. When ligand exchange is slow these may be distinguished by ^1H NMR (but not IR) spectroscopy, but on warming the resonances due to the CNMe and C_5H_4 ligands, and the A-B moiety coalesce. Ligand site exchange probably takes place by the Cotton–Adams mechanism [1] via non-bridged intermediates, with the limitations which result from the imposed *cis* conformation, as is illustrated in Fig. 1. These limitations have much more marked consequences in the $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-}A\text{-}B\text{-}C_5H_4\}(CO)_2(CNMe)_2]$ derivatives, as it has not been previously recognized that the Cotton–Adams mechanism predicts that two non-interconverting forms of these are possible (Fig. 1). Both have been isolated for the first time in the present work. For example, when A-B = $CH_2C(O)$ one is $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2C(O)C_5H_4\}(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe)]$. This exists as a mixture of two isomers (see above) in solution which are rapidly interconverted at higher temperatures. The other is found only as $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2C(O)C_5H_4\}(CO)_2(\mu\text{-}CNMe)_2]$ in toluene solution (and the solid state) but as a mixture of this and $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2C(O)C_5H_4\}(CNMe)_2(\mu\text{-}CO)_2]$ in acetonitrile solution. Similar behaviour has

Table 6
^1H NMR spectra of the $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-}A\text{-}B\text{-}C_5H_4\}(CO)(L)(\mu\text{-}CO)_{2-n}(\mu\text{-}CNMe_2)_n][Y]_n$ salts in CD_3CN solution at 293 K

L [a]	*n*	Y	Resonances [b]				
			C_5H_4 [c]	$CNMe_2$	CNMe	CHCH or CH_2	NMe_2/NMe_3
A-B = *R*,*S*-$CH(NMe_2)CH(NMe_2)$							
CO [d]	1	I	5.37(2) 5.54(2)	4.31(6)		3.48(2)	NMe_2 2.25(12)
(ma)			5.73(2) 6.11(2)				
CO [d]	1	I	5.24(2) 5.46(2)	4.38(6)		3.14(2)	NMe_2 2.35(12)
(mi)			5.73(2) 5.92(2)				
A-B = *R*,*S*-$CH(NMe_2)CH(NMe_3)^+ [SO_3CF_3]^-$							
CO [e]	1	$SO_3CF_3.2H_2O$	5.40(1) 5.63(2)	4.10(3)		3.93(d, 2)	NMe_2 2.19(3, br)
(ma)			5.80(2) 5.85(1)	4.11(3)		4.55(d, 1)	2.52(3, br)
			6.17(1) 6.24(1)			(*J*(AB) = 6.5)	NMe_3 3.00(9)
CO [e]	1	$SO_3CF_3.2H_2O$	5.36(1) 5.52(1)	4.07(3)		3.97(d, 1)	NMe_2 2.19(br, 3)
(mi)			5.65(1) 5.71(1)	4.08(3)		4.50(d, 1)	2.52(br, 3)
			5.91(1) 5.96(1)			(*J*(AB) = 6.1)	NMe_3 2.98(9)
			6.01(1) 6.21(1)				
CO	2	$[SO_3CF_3]_2.2H_2O$	5.80(1) 5.93(1)	4.11(3)		3.99(d, 1)	NMe_2 2.17(3)
			6.05(1) 6.23(1)	4.12(3)		4.57(d, 1)	2.57(3)
			6.33(1) 6.52(1)	4.13(3)		(*J*(AB) = 6.3)	NMe_3 3.00(9)
			6.60(2)				
A-B = $CH_2C(O)$							
CO [f]	1	$SO_3CF_3.2H_2O$	5.47(1) 5.48(1)	4.30(3)		2.87(d, 1)	
			5.51(1) 5.84(1)	4.36(3)		3.58(d, 1)	
			5.91(1) 6.03(1)			($J_{(AB)}$ = 13.4)	
			6.11(1) 6.31(1)				
CO	1	I	5.30(1) 5.58(1)	4.13(3)		3.00(d, 1)	
			5.72(1) 5.77(1)	4.21(3)		3.28(d, 1)	
			5.86(1) 6.03(2)			(J_{AB} 13.6)	
			6.20(1)				
CNMe [g]	1	SO_3CF_3	5.10(1) 5.16(1)	4.06(3)	3.06(3)	2.84(1, d)	
(ma)			5.52(2) 5.58(2)	4.17(3)		2.92(1, d)	
			5.89(1) 5.94(1)			($J_{(AB)}$ = 13.0)	
CNMe [g]		SO_3CF_3	5.05(1) 5.48(1)	4.08(3)	3.06(3)	2.78(1, d)	
(mi)			5.45(1) 5.63(1)	4.13(3)		2.93(1, d)	
			5.70(2) 5.75(1)			($J_{(AB)}$ = 12.7)	
			6.03(1)				
CO [f]	2	$SO_3CF_3.2H_2O$	5.56(2) 6.10(2)	4.07(6)		3.09(2)	
			6.40(2) 6.49(2)	4.15(6)			

[a] (ma) and (mi) indicates major and minor isomers respectively.
[b] Chemical shifts given as ppm downfield from Me_4Si as an internal standard. Resonances are singlets unless it is stated otherwise. d = doublet, m = multiplet, and br = broad. Integrations are given in parentheses. Coupling constants *J* are quoted in Hz..
[c] All C_5H_4 resonances are multiplets.
[d] CD_2Cl_2 solution. (ma): (mi) = 62 : 38.
[e] (ma) : (mi) = 57 : 43.
[f] $CDCl_3$ solution.
[g] $CDCl_3$ solution. (ma) : (mi) = 58 : 42.

Table 7
Crystal data for R,S-[$Fe_2\{\eta,\eta$-$C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu$-$CNMe)_2$]

Crystal size (mm^3)	0.45 × 0.38 × 0.50
Formula	$C_{22}H_{28}N_4O_2Fe_2$
M (a.m.u.)	492.183
Monoclinic	
Space group	$P2_1/n$
a (Å)	8.833(2)
b (Å)	23.700(4)
c (Å)	10.439(3)
β (°)	94.18
U (Å^3)	2179
Z	4
Dc (g cm^{-3})	1.50
μ (cm^{-1})	12.86
F000	1024
Radiation Mo Kα	
Graphite Monochromator	λ = 0.71069 Å
Diffractometer	Hilger Y290
Orienting reflections, range	12, 13 < θ < 20°
Temperature(°C)	22
Scan method	$\omega - 2\theta$
Data collection range	4 < 2θ < 44°
No. unique data	1835
Total $I > 3\sigma I$	1606
No of parameters fitted	181
R [a], R_w [b]	6.22%, 6.85%
Quality-of-fit indicator [c]	1.005
Largest shift/esd, final cycle	< 0.001
Largest positive peak (e|A^{-3})	0.45
Largest negative peak (e|A^{-3})	−0.25

[a] $R = [\Sigma \| F_o | - | F_c \|] / \Sigma | F_o |$.
[b] $R_w = [[\Sigma_w(| F_o - F_c |)^2] / [\Sigma_w(| F_o |)^2]]^{1/2}$; $w = /[(\sigma F_o)^2 - 0.00\underline{155} * F_o^2]$.
[c] Quality-of-fit = $[\Sigma_w(| F_o | - | F_c |)^2 / (\text{Nobs-Nparameters})]^{1/2}$.

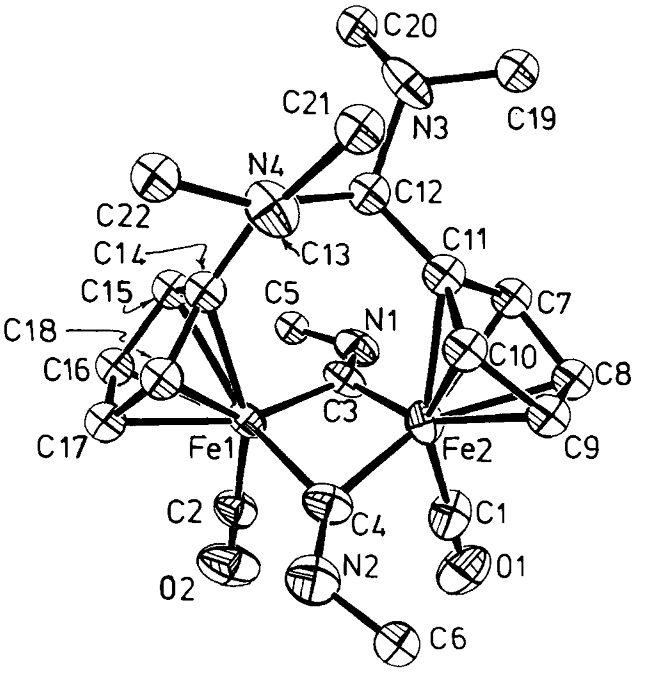

Fig. 3. Structure and atom labelling of R,S-[$Fe_2\{\eta,\eta$-C_5H_4-$CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu$-$CNMe)_2$].

Table 8
Fractional atomic coordinates for R,S-[$Fe_2\{\eta,\eta$-$C_5H_4CH(NMe_2)$-$CH(NMe_2)C_5H_4\}(CO)_2(\mu$-$CNMe)_2$] with estimated standard deviations in parentheses.

Atom	x	y	z
Fe(1)	0.21458(16)	0.16608(5)	0.41695(12)
Fe(2)	−0.02441(17)	0.15008(6)	0.27797(14)
O(1)	−0.2313(11)	0.2241(4)	0.4023(10)
O(2)	0.1128(12)	0.2437(4)	0.6035(9)
N(1)	0.1284(11)	0.2571(4)	0.2258(8)
N(2)	0.0020(12)	0.0903(4)	0.5302(9)
C(1)	−0.1519(14)	0.1945(5)	0.3522(12)
C(2)	0.1538(13)	0.2149(4)	0.5302(10)
C(3)	0.1160(12)	0.2128(4)	0.2848(9)
C(4)	0.0400(13)	0.1197(4)	0.4443(10)
C(5)	0.2481(16)	0.2989(5)	0.2496(14)
C(6)	−0.1399(22)	0.0604(7)	0.5294(16)
N(3)	0.2746(11)	0.0955(4)	−0.0379(9)
N(4)	0.3241(10)	0.0203(4)	0.2148(8)
C(7)	−0.0328(14)	0.1491(5)	0.0748(11)
C(8)	−0.1776(17)	0.1344(6)	0.1204(12)
C(9)	−0.1552(15)	0.0842(6)	0.1950(13)
C(10)	−0.0003(13)	0.0686(5)	0.1952(10)
C(11)	0.0760(11)	0.1080(4)	0.1221(9)
C(12)	0.2381(12)	0.1113(4)	0.0934(9)
C(13)	0.3516(11)	0.0802(4)	0.1899(9)
C(14)	0.3668(10)	0.1123(4)	0.3182(8)
C(15)	0.4306(13)	0.1675(4)	0.3343(10)
C(16)	0.4459(12)	0.1788(4)	0.4666(10)
C(17)	0.3955(14)	0.1326(5)	0.5321(11)
C(18)	0.3464(12)	0.0912(4)	0.4418(10)
C(19)	0.1464(17)	0.0909(6)	−0.1293(14)
C(20)	0.3932(16)	0.1313(5)	−0.0829(12)
C(21)	0.2768(14)	−0.0131(5)	0.1015(11)
C(22)	0.4631(15)	−0.0055(5)	0.2712(12)

been observed when A-B = R,S and $R,R/S,S$-CH(NMe$_2$)CH(NMe$_2$), and CH$_2$CH(NMe$_2$) even though the isomers were not separated in the last compound.

Table 9
Selected bond lengths and bond angles for R,S-[$Fe_2\{\eta,\eta$-C_5H_4-$CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu$-$CNMe)_2$] with estimated standard deviations in parentheses

Bond lengths (Å)			
Fe1–Fe2	2.502(2)	Fe2–C1	1.763(13)
Fe1–C2	1.767(11)	Fe2–C3	1.935(10)
Fe1–C3	1.926(10)	Fe2–C4	1.926(11)
Fe1–C4	1.930(11)	C1–O1	1.145(14)
C2–O2	1.105(13)	C4–N2	1.205(13)
C3–N1	1.225(13)	C6–N2	1.438(18)
C5–N1	1.462(15)		
Bond angles (degrees)			
C2–Fe1–Fe2	101.7(4)	C1–Fe2–Fe1	101.2(4)
C3–Fe1–C2	87.6(5)	C3–Fe2–C1	87.3(6)
C4–Fe1–C2	89.4(4)	C4–Fe2–C1	89.1(6)
C4–Fe1–C3	96.3(5)	C4–Fe2–C3	96.1(4)
Fe1–C2–O2	177.0(10)	Fe2–C1–O1	178.0(10)
Fe1–C3–N1	143.1(9)	Fe2–C3–N1	136.0(8)
Fe1–C4–N2	135.2(9)	Fe2–C4–N2	144.0(10)
Fe1–C3–Fe2	80.8(4)	Fe1–C4–Fe2	80.9(4)
C3–N1–C5	126.0(10)	C4–N2–C6	125.0(10)

These observations provide unambiguous evidence for the validity of the Cotton–Adams rules.

Although inversion at the N atom of the μ-CNMe ligand has been slowed in related systems (Ref. 2 and references therein), it appears to be fast even at −90°C for the complexes reported here. However, we cannot be completely sure, since at such temperatures the spectra are often of poor quality due to solubility problems, and also very complicated, with a plethora of weak resonances as other fluxional processes within the Fe_2L_4 and A-B moieties are slowed.

Coalescence temperatures T_c were used to calculate the activation energies, $\Delta G^\ddagger_{Tc}$, for the various fluxional processes [21]. As implied above, fast ligand site exchange causes coalescence not only of CNMe resonances but also of those due to the C_5H_4 and A-B moieties. For example the CH_2 protons of $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2C(O)C_5H_4\}(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe)]$ gives rise to two doublets at 243 K, which coalesce on warming to a singlet as exchange between the two μ sites becomes fast. The CH_2 protons of the two $[Fe_2\{\eta,\eta\text{-}C_5H_4CH_2C(O)C_5H_4\}(CO)(CNMe)(\mu\text{-}CO)_2]$ isomers are both singlets at 243 K; by 293 K they have coalesced due to fast ligand exchange between the two *t* sites. At still higher temperatures there is a single CH_2 resonance as a consequence of fast μ-*t* site exchange. Of course these separate coalescences are a result of the same ligand exchange process outlined in Fig. 1, but their presence does allow the estimation of $\Delta G^\ddagger_{Tc}$ for this process even when direct measurement from CNMe resonances is impossible owing to experimental difficulties.

The $\Delta G^\ddagger_{Tc}$ for ligand site exchange (Table 10) have values that are generally higher than those obtained for the corresponding processes in their $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ counterparts, which are ca. 14 kcal mol^{-1} ($n = 1$) and ca. 18 kcal mol^{-1} ($n = 2$) [22]. This probably reflects the nature of the bridge-terminal exchange process which, after bridge-opening, proceeds via two non-bridged intermediates that can only undergo interconversion by a rotation about the Fe–Fe bond that eclipses the two cyclopentadienyl groups. As has been suggested by Mann et al. [22] this is probably a sterically demanding, high-energy process. Furthermore it is possible that the partial rotation about the Fe–Fe bond is accompanied by partial rotation about the ring-linking C–C bond, and the steric factors involved in this may account for the increase of $\Delta G^\ddagger_{Tc}$ for μ-*t* site exchange along the series A-B = $CH_2C(O)$ < *R,S*-$CH(NMe_2)CH(NMe_2)$ < *R,R/S,S*-$CH(NMe_2)CH(NMe_2)$, increases which are probably real.

Table 10
Energies of activation ΔG_{Tc} calculated from coalescence temperatures T_c for ligand site-exchange in the $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_{4-n}(CNMe)_n]$ complexes

n	Sites	T_c (K)	ΔG_{Tc} (kcal mol^{-1})
A-B = *R,S*-$CH(NMe_2)CH(NMe_2)$			
1 [a]	$t - t$	316	17.1
1 [b]	$\mu_a - \mu_b$	321	from μ_a 17.7 from μ_b 17.5
1 [c]	$\mu_b - t$	341	from t 17.5 from μ_b 17.2
2 [b,d]	$\mu - \mu$	378	20.6
A-B = *R,R/S,S*-$CH(NMe_2)CH(NMe_2)$			
1 [c]	$\mu - t$	343, 345, 348	19.4
A-B = $CH_2C(O)$			
1 [b]	$\mu - \mu$	280	14.0
1 [c]	$\mu - t$	313	from t 14.5 from μ 14.7
2 [b,e]	$\mu_a - \mu_b$	349	from μt_a 19.1 from μt_b 18.7

[a] $t - t$ exchange; [b] $\mu - \mu$ exchange; [c] $\mu - t$ exchange; [d] $\mu - \mu$ isomer; [e] $\mu - t$ isomer.

3.3. Structure of *R,S*-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CNMe)_2]$

The structure and atom labelling are illustrated in Fig. 3. Bond lengths and angles are summarised in Table 9. The structure is based on those of *R,S*-$[Fe_2\{\eta,\eta\text{-}C_5H_4CH(NMe_2)CH(NMe_2)C_5H_4\}(CO)_2(\mu\text{-}CO)_2]$ [23] and *cis*-$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)_2]$ [19], and contains no unusual molecular dimensions. The configuration of the *R,S*-$CH(NMe_2)CH(NMe_2)$ moiety is unchanged during the substitution of CO by CNMe.

3.4. The reactions of $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_3(CNMe)]$ with alkylating agents

An important aspect of the chemistry of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ complexes is their reaction with alkylating agents such as RI or $ROSO_2CF_3$ to give salts containing the $\mu\text{-}CN(R)Me^+$ ligand [10]. The $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_{4-n}(CNMe)_n]$ derivatives react similarly to give $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_2(\mu\text{-}CO)\{\mu\text{-}CN(R)Me\}]^+$ salts when $n = 1$, and, when $n = 2$, $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)(CNMe)(\mu\text{-}CO)\{\mu\text{-}CN(R)Me\}]^+$ salts from $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe)]$ and $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_2\{\mu\text{-}CN(R)Me\}_2]^{2+}$ salts from $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)_2(\mu\text{-}CNMe)_2]$. However, when A-B = $CH(NMe_2)CH(NMe_2)$ one of the NMe_2 groups may also be alkylated to NMe_2R^+ at the same time, but this can be controlled as alkylation of the CNMe ligand is the faster of the two reactions, especially when RI are the alkylating reagents.

The IR spectra of these compounds between 1550 and 2200 cm^{-1} (Table 4) are very similar to those of their $\eta\text{-}C_5H_5$ counterparts [10] and need no further discussion. The ^1H NMR spectra of the $[Fe_2\{\eta,\eta\text{-}C_5H_4\text{-A-B-}C_5H_4\}(CO)(L)(\mu\text{-}CO)_{2-n}(\mu\text{-}CNMe_2)_n]^{m+}$

salts (Table 6) are unexceptional (cf. Ref. [10]), but not simple as a consequence of the linking group A-B (see above). In most instances each μ-CNMe$_2$ ligand gives rise to two Me resonances as these methyl groups are not equivalent; when A-B = *R*,*S*-CH(NMe$_2$)CH(NMe$_2$) they are equivalent at room temperature but not at low temperature owing to the partial rotation about the ring-linking C–C bond. The presence of the μ-CNMe$_2$ groups prevents exchange of μ and *t* ligands [10], but it does not affect fluxional processes within the ring-linking group A-B [5] which have $\Delta G^{\ddagger}_{\mathrm{Tc}}$ values comparable to those of their tetracarbonyl precursors (see above).

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