The preparation and spectra of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_{4-n}$(CNAr)$_n$] complexes. The reaction of [Fe(CO)$_{5-m}$(CNAr)$_m$] with dicyclopentadiene

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Abstract

The relatively elusive [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_{4-n}$(CNAr)$_n$] complexes where $n = 1$ or 2 and Ar = C$_6$H$_5$, 2-MeC$_6$H$_4$, 4-MeC$_6$H$_4$, 2,4-Me$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$ and 2,4,6-Me$_3$C$_6$H$_2$ have been prepared by two effective, but not completely general routes. One is the light-catalyzed substitution of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_4$] by ArNC which gives the derivatives where $n = 1$ or 2 and, eventually, 4. The other is the reaction at 145 °C of dicyclopentadiene with [Fe(CO)$_5$] and ArNC or with [Fe(CO)$_4$(CNAr)], but not with [Fe(CO)$_3$(CNAr)$_2$] or [Fe(CO)$_4$(CNMe)]. The pathway of the reaction of dicyclopentadiene with [Fe(CO)$_5$] or [Fe(CO)$_4$(CNAr)]] is discussed and it is concluded that it does not proceed via cyclopentadiene and mononuclear cyclopentadienyl complexes but via species containing dicyclopentadiene and two metal atoms which are formed at an early stage in the reaction and which remain associated throughout the reaction up to the formation of the [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_{4-n}$(CNAr)$_n$] derivatives. The infrared and ^{1}H NMR spectra of the complexes are reported and discussed.

Introduction

The thermal reaction of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_4$] with MeNC proceeds in clearly defined steps to give each of the [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_{4-n}$(CNMe)$_n$] ($n = 1$–4) in turn [1]. In contrast similar reactions with aryl isocyanides, ArNC, give only [Fe$_2$(η-C$_5$H$_5$)$_2$(CNAr)$_4$] [2] and it is only for PhNC that the intermediate [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_{4-n}$(CNPh)$_n$] ($n = 1$, 2 or 3) have been obtained [3, 4].

We wanted to prepare [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_{4-n}$(CNAr)$_n$] complexes where $n < 4$ and now report two effective, but not completely general routes. One is the light-catalyzed substitution of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_4$] by ArNC which gives the derivatives where $n = 1$ or 2 and, eventually, 4. The other is the reaction at 145 °C of dicyclopentadiene with [Fe(CO)$_5$] and ArNC or with [Fe(CO)$_4$(CNAr)]. The latter sheds some light on the reaction of dicyclopentadiene with [Fe(CO)$_5$] itself.

There has been a preliminary report of some of this work [5].

Experimental

Previously published methods were used to prepare CNAr (Ar = C$_6$H$_5$, 2-MeC$_6$H$_4$, 4-MeC$_6$H$_4$, 2,4-Me$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$ and 2,4,6-Me$_3$C$_6$H$_2$ [6], [Fe(CO)$_4$(CNAr)] and Fe(CO)$_3$(CNAr)$_2$ [7], and [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_4$] [8]. Other chemicals were purchased and used as received.

Unless it is stated otherwise all reactions were carried out at room temperature under an atmosphere of nitrogen in solvents which had been dried and deoxygenated by refluxing over calcium hydride and distilled before use.

Infrared spectra were run on a Perkin-Elmer 1710 FT-IR spectrometer. ^{1}H NMR spectra were run on a JEOL JNM-GX270 FT-NMR spectrometer using Me$_4$Si as an internal standard.

Elemental analyses were carried out by the Analytical Laboratory of University College, Dublin.

Photolytic reaction of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_4$] with ArNC

A solution of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_4$] (3 mmol) and ArNC (10 mmol) in tetrahydrofuran (60 ml) was stirred. No reaction took place in the dark, but in ambient light a slow reaction gave [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_{4-n}$(CNAr)$_n$] over a period of 1–2 days

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for all ArNC except C_6H_5NC where UV radiation was necessary and reaction time was reduced to 1–2 h. The reactions were monitored by IR spectroscopy. When they were complete the mixtures were filtered, their solvents removed at reduced pressure, and the residues chromatographed on alumina using benzene–hexane mixtures as eluants. The products were further purified by recrystallization from toluene–hexane mixtures. The product yields are given in Table 1.

Thermal reaction of dicyclopentadiene with [Fe(CO)₅] and ArNC

Dicyclopentadiene (80 mmol), $[Fe(CO)_5]$ (40 mmol) and ArNC (20 mmol) were heated in an oil bath at 145 °C for 15–20 h. The reactions were monitored by IR spectroscopy and when complete they were worked-up as described above. The yields of the products are given in Table 1.

Thermal reaction of dicyclopentadiene with [Fe(CO)₄(CNAr)]

Dicyclopentadiene (70 mmol) and $[Fe(CO)_4-$ $(CNAr)]$ (5 mmol) were heated in an oil bath at 145 °C for 20 h. The reactions were monitored by IR spectroscopy and when complete they were worked-up as described above. The yields of the products are given in Table 1.

The compounds prepared, their melting points and their analyses are given in Table 2, their IR spectra in Tables 3 and 4, and their ^1H NMR spectra in Table 5.

Results and discussion

The $[Fe_2(\eta-C_5H_5)_2(CO)_{4-n}(CNAr)_n]$ complexes ($n = 1$ or 2) are purple to red crystalline solids soluble in most organic solvents. They are air-stable in the solid state but are oxidized slowly in solution. They remain unchanged on heating them in xylene, but if excess ArNC is present they rapidly undergo further CO substitution to $[Fe_2(\eta-C_5H_5)_2(CNAr)_4]$.

They may be prepared by: (a) the photolytic reaction of ArNC with $[Fe_2(\eta-C_5H_5)_2(CO)_4]$ at room temperature, (b) the thermal reaction of ArNC with dicyclopentadiene and $[Fe(CO)_5]$ at 145 °C, (c) the thermal reaction of $[Fe(CO)_4(CNAr)]$ with dicyclopentadiene at 145 °C. The last two are closely connected and will be discussed together. All three reactions have their limitations as none give $[Fe_2(\eta-C_5H_5)_2(CO)_2(CNAr)_2]$ where the ArNC ligands have two o-alkyl substituents.

Method (a). The reaction of $[Fe_2(\eta-C_5H_5)_2(CO)_4]$ with ArNC in xylene at 140 °C gives only the $[Fe_2(\eta-C_5H_5)_2(CNAr)_4]$ complexes [2] but at room temperature a much slower reaction occurs and mixtures of the $[Fe_2(\eta-C_5H_5)_2(CO)_{4-n}(CNAr)_n]$ derivatives where $n = 1$ or 2 may be obtained. The reactions are photochemical and do not take place in the dark. When $Ar = C_6H_5$ UV radiation is necessary, but ordinary daylight is adequate in most instances although all reactions to go faster with UV irradiation. More intense radiation, e.g. bright sunlight, brings about rapid further substitution to give ultimately $[Fe_2(\eta-C_5H_5)_2(CNAr)_4]$ derivatives. The relative yield of the products is a function of Ar (Table 1) with the less hindered C_6H_5NC, $2\text{-}MeC_6H_4NC$ and $4\text{-}C_6H_4NC$ giving $[Fe_2(\eta-C_5H_5)_2(CO)_2(CNAr)_2]$ complexes and the more hindered $2,4\text{-}Me_2C_6H_3NC$, $2,6\text{-}Me_2C_6H_3NC$ and $2,4,6\text{-}Me_3C_6H_2NC$ giving the less highly substituted $[Fe_2(\eta-C_5H_5)_2(CO)_3(CNAr)]$ derivatives only.

Methods (b) and (c). $[Fe_2(\eta-C_5H_5)_2(CO)_4]$ is best prepared by the reaction of $[Fe(CO)_5]$ with dicyclopentadiene at 145 °C [8]. Addition of ArNC to such a reaction mixture results in the formation of

TABLE 1. Product yields from various reactions[a] described in the text

ArNC	Yield (%)		
	$[Fe_2(\eta-C_5H_5)_2(CO)_4]$	$[Fe_2(\eta-C_5H_5)_2(CO)_3(CNAr)]$	$[Fe_2(\eta-C_5H_5)_2(CO)_2(CNAr)_2]$
C_6H_5NC	(a) = n.a., (b) = 40, (c) = <5	(a) = 0, (b) = 40–50, (c) = 10	(a) = 60–70, (b) = 5–10, (c) = 50
$4\text{-}MeC_6H_4NC$	(a) = n.a., (b) = 40, (c) = <5	(a) = 0, (b) = 40–50, (c) = 10	(a) = 60–70, (b) = 5–10, (c) = 50
$2\text{-}MeC_6H_4NC$	(a) = n.a., (b) = 40, (c) = <5	(a) = 0, (b) = 50, (c) = 10	(a) = 60–70, (b) = 0, (c) = 50
$2,4\text{-}Me_2C_6H_3NC$	(a) = n.a., (b) = 40, (c) = <5	(a) = 70, (b) = 50, (c) = 50	(a) = 0, (b) = 0, (c) = trace
$2,6\text{-}Me_2C_6H_3NC$	(a) = n.a., (b) = 20, (c) = <5	(a) = 70, (b) = 65, (c) = 70	(a) = 0, (b) = 0, (c) = 0
$2,4,6\text{-}Me_3C_6H_2NC$	(a) = n.a., (b) = 35, (c) = <5	(a) = 70, (b) = 60, (c) = 75	(a) = 0, (b) = 0, (c) = trace

[a]Reaction (a) $[Fe_2(\eta-C_5H_5)_2(CO)_4] + ArNC$ on photolysis; n.a. = not applicable. Reaction (b), $[Fe(CO)_5] + C_{10}H_{12} + ArNC$ at 145 °C; <5% $[Fe(CO)_3(CNAr)_2]$ are always formed in these reactions. Reaction (c), $[Fe(CO)_4(CNAr)] + C_{10}H_{12}$ at 145 °C. Trace = product detected by IR spectroscopy but not isolated.

TABLE 2. Melting points and analyses of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNAr)_n]$ compounds described in the text

Compound	Melting point[a] (°C)	Analyses: found (calc.) (%)		
		C	H	N
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNC_6H_5)]$	120–122	56.0(55.9)	3.7(3.5)	3.3(3.3)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNC_6H_4Me\text{-}4)]$	116–118	56.9(56.9)	3.9(3.8)	3.2(3.2)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNC_6H_4Me\text{-}2)]$	120–122	57.0(56.9)	4.0(3.8)	3.2(3.2)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNC_6H_3Me_2\text{-}2,4)]$	140–143	58.3(57.8)	4.4(4.2)	3.1(3.1)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNC_6H_3Me_2\text{-}2,6)]$	dec. 157	57.6(57.8)	4.2(4.2)	3.0(3.1)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNC_6H_2Me_3\text{-}2,4,6)]$	dec. 155	58.2(58.6)	4.5(4.5)	2.9(3.0)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNC_6H_5)_2]$	150–152	61.7(61.9)	4.0(4.0)	5.5(5.6)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNC_6H_4Me\text{-}4)_2]$	155–157	63.3(63.2)	4.5(4.5)	5.0(5.3)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNC_6H_4Me\text{-}2)_2]$	147–149	63.0(63.2)	4.3(4.5)	5.1(5.3)

[a]Determined in sealed tubes; dec. = melts with decomposition.

small amounts (<5%) of $[Fe(CO)_3(CNAr)_2]$ and a mixture of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNAr)_n]$ complexes where $n=0$, 1 and 2. However the yields of the derivatives where $n=2$ are always low (Table 1).
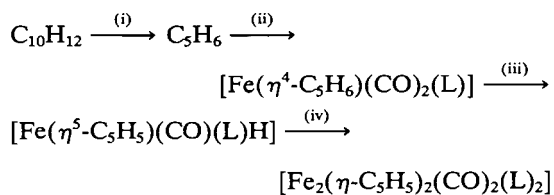
There are two possible routes for this reaction: (i) the formation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ and its subsequent substitution by ArNC to $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNAr)_n]$ ($n=1$ or 2); (ii) the formation of $[Fe(CO)_{5-m}(CNAr)_m]$ complexes and their subsequent reaction with dicyclopentadiene.

It was to test the viability of route (ii) that the reactions of $[Fe(CO)_{5-m}(CNAr)_m]$ with dicyclopentadiene at 145 °C were investigated. All $[Fe(CO)_4(CNAr)]$ gave traces of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ together with mixtures of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNAr)_n]$ complexes where $n=1$ or 2, although it was only for the less bulky C_6H_5NC, $4\text{-}MeC_6H_4NC$ and $2\text{-}MeC_6H_4NC$ that significant amounts of the disubstituted derivatives ($n=2$) were obtained (Table 1). No reaction took place between dicyclopentadiene and any $[Fe(CO)_3(CNAr)_2]$ or $[Fe(CO)_4(CNMe)]$. As the further substitution of $[Fe(CO)_3(CNAr)_2]$ was known to be difficult [7], the reactions of $[Fe(CO)_{5-m}(CNAr)_m]$ ($m>2$) were not investigated.

It is probable that the reaction used in method (b) proceeds largely via route (ii). The reactions of $[Fe(CO)_5]$ with ArNC are complete within 4 h at 70 °C [7]; that with dicyclopentadiene is much slower [8]. Consequently significant amounts of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ would only be formed after all of the ArNC had been consumed by the large excess of $[Fe(CO)_5]$ giving $[Fe(CO)_4(CNAr)]$ and a little $[Fe(CO)_3(CNAr)_2]$. Furthermore, if reaction (b) was carried out at temperatures below 140 °C, the only products were $[Fe(CO)_{5-m}(CNAr)_m]$.

Reaction of dicyclopentadiene with $[Fe(CO)_5]$ and $[Fe(CO)_4(CNAr)]$

The reaction of $C_{10}H_{12}$ with $[Fe(CO)_5]$ takes place at 140–145 °C with no significant reaction at lower temperatures whilst at higher temperatures decomposition becomes important. It has been assumed that the reaction takes place as shown below where L = CO with the formation in turn of cyclopentadiene, $[Fe(\eta^4\text{-}C_5H_6)(CO)_3]$, $[Fe(\eta^5\text{-}C_5H_5)(CO)_2H]$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ [9]. $[Fe(CO)_4(CNAr)]$ may also react similarly to give $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNAr)_n]$ ($n=1$ or 2) with the understanding that the ligands lost in either step (ii) or (iii) may be CO or CNAr.

$$C_{10}H_{12} \xrightarrow{(i)} C_5H_6 \xrightarrow{(ii)}$$
$$[Fe(\eta^4\text{-}C_5H_6)(CO)_2(L)] \xrightarrow{(iii)}$$
$$[Fe(\eta^5\text{-}C_5H_5)(CO)(L)H] \xrightarrow{(iv)}$$
$$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(L)_2]$$

There are a number of difficulties associated with this proposal. The most important is that the first step, the reverse Diels–Alder reaction of dicyclopentadiene does not take place until c. 180 °C. At 140 °C the interconversion of exo and endo-$C_{10}H_{12}$ without monomerization becomes rapid via, it is suggested, a diallylic diradical (Fig. 1) [10]. A further objection to the proposed pathway is that the formation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNAr)]$ would require the reaction of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2H]$ with $[Fe(\eta^5\text{-}C_5H_5)(CO)(CNAr)H]$ in step (iv). In the case of ArNC being $2,6\text{-}Me_2C_6H_3NC$, for example, where the yield of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNAr)]$ is very high (70% after purification) the two hydrides would have to be formed in almost equal amounts. Also, it would be surprising in such cases if so little $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ were formed at the same time from $[Fe(\eta^5\text{-}C_5H_5)(CO)_2H]$, especially as all three $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNC_6H_5)_n]$ ($n=0$, 1 and 2) are

TABLE 3. IR spectra of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNAr)]$ complexes described in the text

CNAr	Solvent	Absorption bands[a,b]						
		A	B	C	D	E	F	G
CNC$_6$H$_5$	hexane	1699(3.2)		1804(4.4)	1957(12.1)	1975(1.6)	2002(10)	
	CS$_2$	1698(3.4)		1800(8.1)	1953(15.5)	1970(1.4)	1995(10)	
	xylene	1697(4.8)		1803(9.5)	1955(9.5)		1995(10)	
	MeCN	1689(3.1)		1787(1.8)	1947(2.6)		1987(10)	
	KBr	1702(m)		1782(m)	1938(m)		1979(s)	
CNC$_6$H$_4$Me-4	hexane	1704(3.3)	1778(0.8)	1807(5.4)	1955(11.1)	1976(1.1)	2000(10)	2086(0.1)
	CS$_2$	1704(6.1)	1766(1.4)	1798(4.5)	1949(15.6)	1970(1.2)	1993(10)	2084(0.4)
	xylene	1695(5.7)	1768(1.6)	1796(5.3)	1949(8.1)		1993(10)	2087(0.8)
	MeCN	1691(2.6)	1754(1.1)	1785(1.9)	1944(2.7)		1985(10)	2084(0.8)
	KBr	1690(m)		1774(m)	1936(m)		1978(m)	
CNC$_6$H$_4$Me-2	hexane	1704(6.6)	1776(2.3)	1801(10.8)	1956(12.6)	1975(1.9)	2001(10)	2087(0.2)
	CS$_2$	1705(4.9)	1766(3.0)	1798(4.7)	1950(10.4)	1970(sh)	1992(10)	2084(0.5)
	xylene	1705(4.5)	1767(2.8)	1797(4.2)	1948(7.6)		1993(10)	2086(0.8)
	MeCN	1696(3.8)	1753(2.3)	1784(2.8)	1944(4.1)		1985(10)	2084(0.8)
	KBr	1690(m)		1787(m)	1937(s)		1978(m)	
CNC$_6$H$_3$Me$_2$-2,4	hexane	1714(2.8)	1779(1.9)	1805(5.6)	1959(11.9)	1975(1.2)	2001(10)	2086(0.6)
	CS$_2$	1713(4.0)	1767(4.4)	1798(3.7)	1952(9.9)	1971(sh)	1995(10)	2088(1.7)
	xylene	1713(6.8)	1768(7.3)	1797(5.9)	1950(8.9)		1993(10)	2091(1.3)
	MeCN	1709(3.3)	1756(3.5)	1786(2.5)	1946(3.4)		1986(10)	2089(1.8)
	KBr		1740(s)	1778(m)	1949(s)			2079(s)
CNC$_6$H$_3$Me$_2$-2,6	hexane		1777(8.6)		1956(10), 1962(7.0)			2080(1.4)
	CS$_2$		1766(15.6)		1953(10)			2080(4.7)
	xylene		1768(16.1)		1951(10)			2085(6.6)
	MeCN		1756(17.8)	1774(w)	1946(10)			2084(9.7)
	KBr		1744(s)		1948(s)			2086(s)
CNC$_6$H$_2$Me$_3$-2,4,6	hexane		1776(16.5)		1952(10), 1958(7.9)			2087(4.4)
	CS$_2$		1764(14.0)	1774(w)	1951(10)			2083(5.4)
	xylene		1766(20.4)		1950(10)			2088(8.5)
	MeCN		1755(16.8)		1944(10)			2086(12.5)
	KBr		1744(s)	1774(w)	1947(s)			2095(s)

[a]Peak positions (cm^{-1}) with relative peak heights in parentheses; s = strong, m = medium, w = weak and br = broad. [b]Absorption band A due to $\nu(CN_\mu)$ vibrations of III and IV; B to antisymmetric $\nu(CO_\mu)$ of I and IV; C to $\nu(CO_\mu)$ of III; D to antisymmetric $\nu(CO)$ of IV and $\nu(CO)$ of III and IV; E to antisymmetric $\nu(CO)$ of I and II; F to symmetric $\nu(CO)$ of III; G to $\nu(CN)$ of I and II. In solvents other than hexane and CS$_2$, D and E cannot be distinguished.

TABLE 4. IR spectra of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNAr)_2]$ complexes described in the text[a,b]

CNAr	Solvent	Absorption bands					
		H	I	J	K	L	M
CNC_6H_5	hexane	1688(12.6)	1795(1.1)	1952(15.4)	1971(3.8)	1993(10)	2077(1.0)
	CS_2	1684(7.7)	1783(0.5)	1945(6.7)		1988(10)	
	xylene	1683(8.0)	1783(0.5)	1945(5.9)		1987(10)	2073(0.5)
	MeCN	1678(7.4)	1771(0.3)	1942(2.9)		1982(10)	2076(0.4)
	KBr	1687(s, br)		1934(m) 1944(s)			
$CNC_6H_4Me\text{-}4$	hexane	1692(12.5)	1792(1.1)	1950(15.8)	1969(2.5)	1992(10)	2077(0.6)
	CS_2	1686(6.4)	1781(0.5)	1943(8.1)		1987(10)	
	xylene	1685(7.6)	1782(0.3)	1944(5.7)		1985(10)	2074(0.5)
	MeCN	1677(7.2)	1775(0.7)	1941(3.3)		1981(10)	2075(0.9)
	KBr	1669(s, br)		1936(s) 1947(s)			
$CNC_6H_4Me\text{-}2$	hexane	1692(6.2)	1784(1.0)	1952(6.2)	1971(1.9)	1994(10)	2080(0.6)
	CS_2	1690(7.2)	1780(1.2)	1946(5.0)		1988(10)	
	xylene	1691(8.3)	1782(1.9)	1945(5.2)		1987(10)	2085(1.8)
	MeCN	1683(8.3)	1768(1.0)	1940(3.0)		1980(10)	2079(1.7)
	KBr	1690(s, br)		1923, 1929(m)	1969(s)		

[a]Peak positions (cm^{-1}) with relative peak heights in parentheses; s = strong, m = medium, w = weak and br = broad. [b]Absorption band H is due to the $\nu(CN_\mu)$ vibrations of VII, VIII, IX and X; I to the $\nu(CO_\mu)$ of VII and VIII; J to the antisymmetric $\nu(CO)$ of IX and X; K to the $\nu(CO)$ of VII and VIII; L to the symmetric $\nu(CO)$ of IX; M to the $\nu(CN)$ of VII and VIII.

TABLE 5. ^{1}H NMR spectra of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNAr)_n]$ complexes described in the text

CNAr	Temperature (K)	Solvent	Isomer	Resonances[a]	
				C_5H_5	CH_3
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNAr)]$					
CNC_6H_5	303	CD_2Cl_2		4.70	
	248	CD_2Cl_2	III	4.72	
			IV	4.65	
$CNC_6H_4Me\text{-}2$	303	CD_2Cl_2		4.70	2.30
	243	CD_2Cl_2	I/II	4.73, 4.64	2.16
			III	4.71	2.43
			IV	4.62	2.43
$CNC_6H_3Me_2\text{-}2,4$	293	CD_2Cl_2		4.71	2.33, 2.30
	233	CD_2Cl_2	I/II	4.73, 4.68	2.18, 2.15
			III	4.71	2.42, 2.31
			IV	4.63	2.42, 2.29
$CNC_6H_3Me_2\text{-}2,6$	293	CD_2Cl_2		4.71	2.26
	223	CD_2Cl_2	I/II	4.74, 4.70	2.18, 2.15
$CNC_6H_2Me_3\text{-}2,4,6$	293	CD_2Cl_2		4.70	2.19, 2.17
	223	CD_2Cl_2	I/II	4.73, 4.69	2.13, 2.06
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNAr)_2]$					
CNC_6H_5	293	C_6D_6	VII/VIII	4.47, 4.38	
			IX	4.31	
			X	4.43	
$CNC_6H_4Me\text{-}4$	293	C_6D_6	VII/VIII	4.44, 4.54	2.20
			IX	4.38	2.20
			X	4.49	2.20
$CNC_6H_4Me\text{-}4$	293	$CDCl_3$	VII/VIII	4.69, 4.64	2.42, 2.47
			IX	4.67	2.39
			X	4.61	2.37
$CNC_6H_4Me\text{-}2$	293	C_6D_6	VII/VIII	4.50, 4.38	2.56, 2.09
			IX	4.33	2.49
			X	4.43	2.49
$CNC_6H_4Me\text{-}2$	293	$CDCl_3$	VII/VIII	4.69, 4.65	2.56, 2.27
			IX	4.66	2.53
			X	4.60	2.49

[a]Chemical shifts, δ, as ppm downfield from Me_4Si as an internal standard. All resonances are singlets.
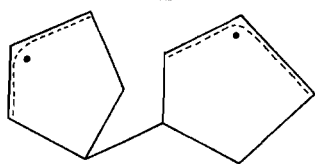

Fig. 1. The proposed diradical intermediate in the non-dissociative *endo–exo* isomerization of dicyclopentadiene [10].

formed together in the reaction of $C_{10}H_{12}$, $[Fe(CO)_5]$ and C_6H_5NC in refluxing xylene (see above). Consequently we conclude that the above pathway is not important. A possible alternative suggestion is that the interaction of two $[Fe(CO)_4(L)]$ with *di-cyclopentadiene* takes place at an early stage. The

two Fe atoms and the C_{10} moiety would then remain associated throughout the reaction up to the formation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNAr)_n]$. A possible intermediate in such a process is the diallylic diradical, mentioned above in connection with *endo–exo* isomerization, which could lead to a C–C linked diallyl–diiron complex with a metal–metal bond (cf. $[Fe_2(\eta\text{-}C_3H_5)_2(CO)_6]$ [11]). Such a suggestion is speculative and awaits a kinetic study, but it is consistent with the above data.

IR and ^{1}H NMR spectra

The spectra show that the $[Fe_2(\eta\text{-}C_5H_5)_2\text{-}(CO)_{4-n}(CNAr)_n]$ complexes exist as a single isomer

in the solid state but as an interconverting equilibrium mixture of isomers in solution. These isomers have structures similar to those of cis- and trans-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CO)$_2$] [12] (cf. cis-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CO)(μ-CN)Ph)] [13] and trans-[Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(μ-CNPh)$_2$] [14]), and their relative proportions in solution are a function of the isocyanide group Ar and the solvent. Similar behaviour has been observed for the closely related [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_3$(CNR)] and [Fe$_2$(η-C$_5$H$_5$)$_2$-(CO)$_2$(CNR)$_2$] derivatives of alkyl isocyanides, RNC, in refs. 15, 16 and 17 where the identification of the intense absorption bands which lie between 1700 and 2200 cm^{-1} in the IR spectra of the complexes and their more detailed assignment to particular μ-CN, μ-CO, CO and CN stretching vibrations of different isomers (four are possible when $n = 1$, and six when $n = 2$ as illustrated in Fig. 2) has been discussed. This assignment is given in Tables 3 and 4 where the frequencies and relative intensities of the various absorption bands are also summarized. Correlation of the IR with the NMR spectra and comparison of the latter with those of the alkyl-isocyanide derivatives [15–17] allow the NMR spectra of the [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_{4-n}$(CNAr)$_n$] complexes to be assigned (Table 5).

In the solid state [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_3$(CNAr)] have similar IR spectra when Ar = C$_6$H$_5$, 4-MeC$_6$H$_4$ and 2-MeC$_6$H$_4$. All are probably the cis μ-CNAr isomer III (cf. [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_3$(CNPh)] [13]). On the other hand the complexes of the more bulky ligands where Ar = 2,4-Me$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$ and 2,4,6-Me$_3$C$_6$H$_2$ are t-CNAr isomers, I or II, but it is not clear which. [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(CNAr)$_2$] have the trans structure X with no terminal CNAr ligands
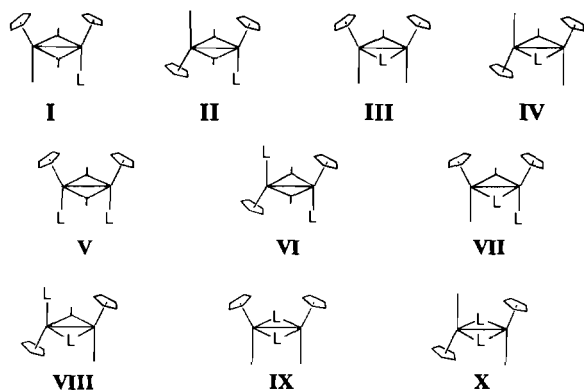
when Ar = C$_6$H$_5$ or 4-MeC$_6$H$_4$ (cf. [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$(CNPh)$_2$] [14]) but is the cis isomer IX when Ar = 2-MeC$_6$H$_4$.

In solution [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_3$(CNAr)] complexes exist as mixtures of isomers which interchange rapidly on the NMR timescale at room temperature or just above. The proportion of the isomers which contain μ-CNAr ligands decrease along the series Ar = C$_6$H$_5$ > 4-MeC$_6$H$_4$ > 2-MeC$_6$H$_4$ > 2,4-Me$_2$C$_6$H$_3$ > 2,6-Me$_2$C$_6$H$_3$ > 2,4,6-Me$_3$C$_6$H$_2$, and solvent = hexane > carbon disulfide > toluene, xylene > acetonitrile. The PhNC complex exists solely as a mixture of III and IV in all solvents, whilst for the bulky 2,6-Me$_2$C$_6$H$_3$NC and 2,4,6-Me$_3$C$_6$H$_2$NC ligands only I and II are found. Thus the μ-CNAr isomers are destabilized with respect to the t-CNAr isomers by more bulky Ar groups, by electron-donating substituents on the aryl ring, and by more polar solvents. Similar behaviour has been observed and rationalized for the related alkyl isocyanide complexes [15–17]. The relative concentrations of III and IV are also influenced by the solvent. The cis isomer III increases in importance with increasing solvent polarity along the series hexane > carbon disulfide > toluene, xylene > CD$_2$Cl$_2$, CDCl$_3$ > acetonitrile as has been observed for [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_4$] [18]. Thus IV is the principal species present in solutions of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_3$(CNPh)] in hexane, but III appears to overwhelmingly predominate in acetonitrile. Solvent polarity also affects the I:II isomer ratio at room temperature, but there is no way of assigning unambiguously the IR absorption bands to either I or II. The ^{1}H NMR spectra of [Fe$_2$(η-C$_5$H$_5$)$_2$-(CO)$_3$(CNAr)] for Ar = 2,6-Me$_2$C$_6$H$_3$ and 2,4,6-Me$_3$C$_6$H$_2$ do not resolve this problem as they show single sets of resonances due to the cyclopentadienyl and Me protons, respectively at room temperature, and cooling splits the former to a 1:1 doublet but leaves the latter unchanged even at 183 K. Similar behaviour has been observed for [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_3$(CNBu-t)] where it was attributed to either very rapid I/II interconversion even at low temperatures [19] or to a shifting of the I/II equilibrium with temperature so that only one is present at low temperatures [16]. For the III/IV interconversion of [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_3$(CNPh)] where the isomer ratio is 2:1 in toluene-D$_8$ solution, $\Delta\nu = 39.7$ Hz, $T_c = 290$ K and $\Delta G_{Tc} = 14.8$ (from cis) or 14.4 (from trans) Kcal mol^{-1} [20]. This is considerably larger than the $\Delta G_{Tc} = c.$ 10.5 Kcal mol^{-1} found for the cis–trans exchange in [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_4$] [21]. The difference is probably due to the strongly electron-withdrawing nature of the phenyl group which makes C$_6$H$_5$NC greatly prefer bridging as opposed to terminal coordination. There is then a greater barrier to formation of the non-bridged intermediate in cis–trans isomer exchange in [Fe$_2$(η-C$_5$H$_5$)$_2$-

Fig. 2. The geometric isomers of the [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_3$(CNAr)] (I–IV) and [Fe$_2$(η-C$_5$H$_5$)$_2$(CO)$_2$-(CNAr)$_2$] complexes (V–X). Fe atoms and CO groups have been omitted for clarity (L = CNAr).

$(CO)_3(CNPh)]$ as compared with $[Fe_2(\eta\text{-}C_5H_5)_2\text{-}(CO)_4]$.

There is no evidence for the presence of isomers **V** and **VI** in solutions of the $[Fe_2(\eta\text{-}C_5H_5)_2\text{-}(CO)_2(CNAr)_2]$ complexes, but exchange of the other isomers (**VII–X**) is slow on the NMR timescale at room temperature and does not become rapid even at 100 °C where decomposition takes place. When $Ar = C_6H_5$ the principal species present are **IX** and **X**, but contrary to previous reports [4] small amounts of **VII** and **VIII** are also present. Their importance increases along the series $Ar = C_6H_5 < 4\text{-}MeC_6H_4 < 2\text{-}MeC_6H_4$ as the increasing ligand bulk and electro-donating substituents destabilize the μ-CNAr isomers, and along the solvent series hexane < carbon disulfide < xylene < chloroform < acetonitrile (cf. above). The ratio of *cis* **IX** to *trans* **X** increases in favour of the former with increasing solvent polarity hexane < carbon disulfide < xylene < acetonitrile so that whereas **X** is the principal species present in solutions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNPh)_2]$ in hexane, **IX** overwhelmingly predominates in acetonitrile. It is not clear from the IR spectra if only one of isomers **VII** and **VIII** is present in the solutions or if both are present but have accidentally coincident $\nu(CO)$ and $\nu(CN)$ absorption bands. However, the ^1H NMR spectra of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNAr)_2]$ $(Ar = 2\text{-}$ or $4\text{-}MeC_6H_4)$ in deuterochloroform show resonances due to the Me groups of **IX** and **X** and two equal resonances due to the Me groups of bridging and terminal CNAr ligands of **VII/VIII**. Therefore the doublet due to the cyclopentadienyl protons of this last pair is unlikely to arise from a rapidly interconverting mixture of *cis* and *trans* **VII** and **VIII** as such an interconversion would require bridge–terminal ligand exchange at the same time [22]. Consequently it is probable that only one of **VII** or **VIII** is present in solution, but it is not clear which.

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