Synthesis of [Fe(η^4-C_8H_8)(CO)$_2$L] [L = MeNC, Pr^{i}NC, Bu^{t}NC, PhNC, 2,6-$Me_2C_6H_3NC$, or P(OMe)$_3$] and Proof of the Applicability of the Woodward–Hoffmann Rules to the Fluxionality of [Fe(η^4-C_8H_8)(CO)$_2$(CNPr^i)]†

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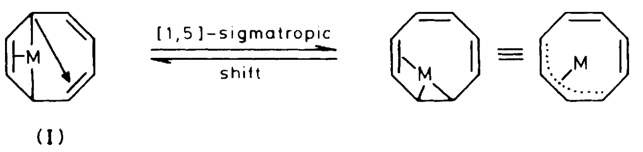
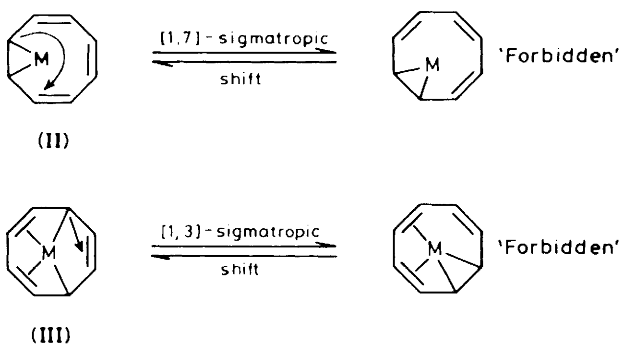
The compounds [Fe(η^4-C_8H_8)(CO)$_2$L] [L = MeNC, Pr^{i}NC, Bu^{t}NC, PhNC, 2,6-$Me_2C_6H_3NC$, or P(OMe)$_3$] have been synthesised and their ^{1}H, ^{13}C, and ^{31}P n.m.r. spectra reported. A detailed study of the fluxionality of [Fe(η^4-C_8H_8)(CO)$_2$(CNPr^i)] has been performed using the DANTE pulse sequence. The mechanism of fluxionality is shown to be consistent with the Woodward–Hoffmann rules and other mechanisms are rejected.

The variability in fluxional behaviour of organometallic compounds was explained in 1977 by Mingos[1] using the Woodward–Hoffman rules and this work has recently been reviewed.[2] The approach is based on a valence-bond description of the bonding in polyene and polyenyl complexes of the transition metals. Thus an η^4-C_8H_8 ring is described as in (**I**) and the observed, 1,2-metal shift is described as a [1,5]-suprafacial sigmatropic shift, with retention of configuration, see Scheme 1. In general, the η^4-C_8H_8 ring is highly fluxional, *e.g.*, for [Fe(η^4-C_8H_8)(CO)$_3$] $\Delta G^‡ = 6.8$ kcal mol^{-1},[3] but the η^2-C_8H_8 rings are generally static,[4] *i.e.* $\Delta G^‡ > 17$ kcal mol^{-1}, or when the η^6-C_8H_8 ring is fluxional the activation energy is relatively high, $\Delta G^‡ > 14$ kcal mol^{-1}, and often undergoes a 1,3-shift. This behaviour is atrributed to the fluxionality of the η^2-C_8H_8, (**II**), and η^6-C_8H_8, (**III**), rings being symmetry forbidden as 1,7- and 1,3-suprafacial sigmatropic shifts are required, see Scheme 2. Similar arguments are used to explain why η^2-C_6R_6 rings are highly fluxional while η^4-C_6R_6 rings are vitually static. Unfortunately the validity of this approach is brought into question by the C_7H_7 ring system. The η^3-C_7H_7 ring is highly fluxional as predicted, with $\Delta G^‡ = 7$—13 kcal mol^{-1},[5] but the η^5-C_7H_7 ring, which should be static, is quite fluxional with $\Delta G^‡ = 11$—16.5 kcal mol^{-1}.[6] The presence of other mechanisms should come as no surprise. Also the validity of the Woodward–Hoffmann rules[7] in organic chemistry is in a large part due to the strength of carbon–hydrogen and carbon–carbon bonds. The fact that the rules are not as rigid in organometallic systems simply reflects the weakness of many metal–carbon bonds.[8]

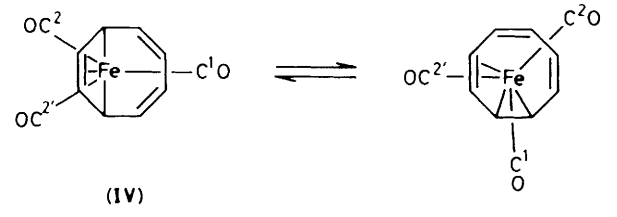
In order to test the validity of the rules, it is necessary to make a prediction which can be tested experimentally. In a ^{13}C n.m.r. study of the fluxionality of [Fe(η^4-C_8H_8)(CO)$_3$], structure (**IV**), Cotton and Hunter[3] noted that exchange of the inequivalent carbonyl groups occurs with the same rate as 1,2-shifts of the η^4-C_8H_8 ring. This observation can be easily explained using the approach outlined in Scheme 1. The iron is then formally six-co-ordinate and the [1,5]-sigmatropic shift would not be expected to disrupt the co-ordination sphere of the iron.[9] As a consequence of the [1,5]-sigmatropic shift, the unique carbonyl group exchanges with the two equivalent carbonyl groups, see Scheme 3. However, this observation does not prove the applicability of the Woodward–Hoffmann mechanism as it is well known that carbonyl group scrambling on [Fe(η^4-diene)(CO)$_3$] molecules is a facile process[10] and the two processes may be accidently degenerate.[3]



Scheme 1.



Scheme 2.



Scheme 3.

This ambiguity may be removed by synthesising a derivative of the type [Fe(η^4-C_8H_8)(CO)$_2$L], when very specific predictions can be made, see Scheme 4. There are now two isomers possible, (**V**) and (**VI**), and three possible situations.

(*i*) The symmetric isomer (**V**) is more stable than the asymmetric isomer (**VI**) to such an extent that (**VI**) does not exist in solution at a detectable concentration. In this case, the activation energy will be increased by the energy difference between (**VI**) and (**V**) and three shifts will be required to return to the original isomer, resulting in an overall 1,4-shift of the metal.

(*ii*) The asymmetric isomer (**VI**) is much more stable than the symmetric isomer (**V**). There will then be a low-energy process

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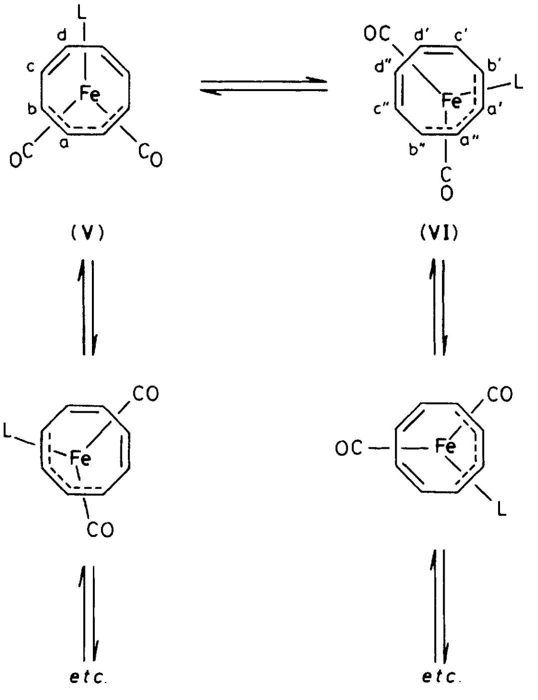
† *Non-S.I. unit employed:* cal = 4.184 J.

where carbon atoms exchange pairwise, see Table 1, but carbon atoms a′ and d″ remain sharp, not being involved in the exchange, see Scheme 4. At higher temperatures, a higher energy process *going via* isomer (**V**) becomes significant permitting total exchange.

(*iii*) Both isomer (**V**) and (**VI**) are present in solution and total exchange is permitted.

There are several compounds of this class in the literature. $[Fe(\eta^4-C_8H_8)(\eta^4-C_4H_6)(CO)]$ has been shown to have structure (**V**)[11] and undergoes 1,2-metal shifts, contrary to the above predictions.[12] However, with an activation energy of *ca.* 13 kcal mol^{-1}, there is sufficient energy for two processes to occur at the same time: 1,5-sigmatropic shift, and a ligand scrambling at the metal. Treatment of $[Fe(\eta^4-C_8H_8)(CO)_3]$ with $[N(SiMe_3)_2]^-$ yields $[Fe(\eta^4-C_8H_8)(CO)_2(CN)]^-$ which reacts with RX (X = Cl, Br, or I) to give $[Fe(\eta^4-C_8H_8)(CO)_2(CNR)]$.[13] These materials were shown to be fluxional, but no mechanisms were reported.



Scheme 4.

Table 1. Predicted exchanges for isomer (**VI**) without interconversion with (**V**)

a′ no exchange
a″ ⇌ b′
b′ ⇌ a″
b″ ⇌ c′
c′ ⇌ b″
c″ ⇌ d′
d′ ⇌ c″
d″ no exchange

Experimental

All preparations and subsequent work-up were carried out under oxygen- and moisture-free conditions. All solvents were dried, distilled, and stored over 4A molecular sieves.

The compound $[Fe(\eta^4-C_8H_8)(CO)_3]$ was prepared by a standard method[14] and purified by sublimation prior to use. Trimethylamine oxide was supplied by the Aldrich Chemical Co. Ltd. as a dihydrate and was dehydrated by benzene azeotropic dehydration in a Dean–Stark apparatus prior to use. The isonitriles were synthesised within this department and the trimethyl phosphite was distilled prior to use.

Infrared spectra were recorded as KBr discs on a Perkin-Elmer 297 infrared spectrometer. The 220-MHz ^1H n.m.r. spectra were recorded on a Perkin-Elmer R34 spectrometer, the 40-MHz ^{31}P n.m.r. spectrum on a JEOL PS-100 spectrometer, and the 100-MHz ^{13}C n.m.r. spectra on a Bruker WH 400 spectrometer. The spin-saturation transfer measurements were performed using the following procedure. The probe temperature was adjusted so that the cyclo-octatetraene carbon atoms were significantly broadened by exchange. The observation frequency was chosen to be coincident with the signal to be inverted. The DANTE pulse sequence was used to apply a specific 180° pulse.[15] The DANTE pulse delay, τ, was chosen to avoid any of the side-bands being coincident with any cyclo-octatetraene carbon signals. The pulse sequence $[5T_1 - (\tau_1 - P1)_{20} - \frac{\pi}{2} - \text{acquire}]_n$ was applied and the length of the DANTE pulse $P1$ adjusted to give maximum signal inversion. The experiment was then performed by introducing a delay, τ_2, for exchange to occur between the DANTE pulse sequence and the $\frac{\pi}{2}$ observing pulse. The experiment was repeated with a range of τ_2 values varying from 1 μs to 1 s. Careful temperature adjustment is essential to balance chemical exchange, spin-lattice relaxation, and line-broadening due to exchange. There is only about a 5 °C working range at −118 °C.

Preparations of $[Fe(\eta^4-C_8H_8)(CO)_2L]$ (L = MeNC, Pr^{i}NC, Bu^{t}NC, PhNC, 2,6-$Me_2C_6H_3NC$, *or* $P(OMe)_3$].—In a typical preparation a round-bottomed three-necked 50-cm^3 flask was charged with $[Fe(\eta^4-C_8H_8)(CO)_3]$ (0.5 g, 2 mmol), CH_3CN (25 cm^3), and ligand (3 mmol) and then Me_3NO (0.23 g, 3 mmol) was added from a side-arm tube. After stirring the mixture for 16 h, during which time CO was replaced by L, the solvent was removed under vacuum (0.1 mmHg/20 °C). The residue was

Table 2. Preparative details of $[Fe(\eta^4-C_8H_8)(CO)_2L]$ [L = MeNC, Pr^{i}NC, Bu^{t}NC, PhNC, 2,6-$Me_2C_6H_3NC$, or $P(OMe)_3$]

				Analysis (%)					
				C		H		N	
L	Yield (%)	M.p (°C)	Eluant*	Found	Calc.	Found	Calc.	Found	Calc.
MeNC	43.0	69	Petrol	56.60	56.10	4.20	4.30	5.55	5.45
Pr^{i}NC	32.5	41—42	Petrol–CH_2Cl_2 (2:1)	58.75	59.00	5.20	5.27	5.15	4.90
Bu^{t}NC	43	100	Petrol	60.00	60.20	5.65	5.70	4.35	4.70
PhNC	35	92—93	Petrol–CH_2Cl_2 (1:1)	64.95	64.00	4.00	4.10	4.15	4.40
2,6-$Me_2C_6H_3NC$	33	94—95	Petrol	65.30	65.70	4.80	4.90	3.90	4.00
$P(OMe)_3$	55	48—49	Petrol–CH_2Cl_2 (1:1)	46.30	45.90	4.90	5.00		

* Petrol = light petroleum (b.p. 40—60 °C).

Table 3. ^{1}H N.m.r., ^{31}P n.m.r., infrared, and mass spectroscopic data for [Fe(η^4-C_8H_8)(CO)$_2$L] [L = MeNC, Pr^{i}NC, Bu^{t}NC, PhNC, 2,6-$Me_2C_6H_3$NC, or P(OMe)$_3$]

	I.r./cm^{-1}				δ(^{1}H)/p.p.m.	
L	ν(C≡O)*	ν(C≡N)	M^+	δ(^{31}P)/p.p.m.	C_8H_8	Other signals
MeNC	1 980s 1 950s 1 930s	2 180	257		5.12	3.30 (s, 3 H, Me)
Pr^{i}NC	1 993s 1 950s 1 943s	2 160	285		5.10	1.27 (d, 6 H, Me), 3.79 [septet, 1 H, CH, ^3J(HH) 8 Hz]
Bu^{t}NC	1 995s 1 980s 1 943s	2 150	299		5.11	1.35 (s, 9 H, Me)
PhNC	1 990s 1 920s	2 130	319		5.18	7.15—7.32 (overlapping peaks, 5 H, Ph)
2,6-$Me_2C_6H_3$NC	1 990s 1 980s 1 950s	2 130	347		5.18	2.33 (s, 6 H, Me), 7.02—7.07 (overlapping peaks, 3 H, $C_6H_3Me_2$)
P(OMe)$_3$	1 990s 1 980s 1 930s		340	133.9	5.15	3.60 [s, 9 H, OMe, ^3J(^{1}H^{31}P) 11 Hz]

* Peak shapes indicate the presence of weaker overlapped bands.

Table 4. Low-temperature ^{13}C n.m.r. spectra of selected resonances of [Fe(η^4-C_8H_8)(CO)$_2$L] in CD_2Cl_2–$CHFCl_2$

			δ/p.p.m.					
				C_8H_8^{a}				
L	θ$_c$/°C	Structure	CO	a	b	c	d	Ratio
2,6-$Me_2C_6H_3$NC	*ca.* −150	**(VI)**	215.5	90.5	57.2	*ca.* 129^b	118.2	3
			217.7	88.7	62.7			
		(V)	218.7	*ca.* 87.5	*ca.* 62	*ca.* 129^b	118.2	1
P(OMe)$_3$	*ca.* −150	**(VI)**	216.0	89.8	58.0	128.6	118.2	
			217.2	87.2	62.4	129.4		
		(V)						none detected
PhNC	−136	**(VI)**	215.6	88.8	57.2	*ca.* 129^b	118.6	1
			217.8	90.6	62.6			
		(V)	218.4	87.4	62.4	*ca.* 129^b	118.6	1
Bu^{t}NC	−142.5	**(VI)**	218.8	91.0	62.4	129.7	117.7	1
			216.7	88.3	55.6	129.1		
		(V)	219.7	86.7	61.1	127.4	118.3	2
MeNC	−142.6	**(VI)**	218.7	90.7	62.1	129.7	117.8	3
			216.4	88.3	55.6	128.9		
		(V)		*ca.* 87.4	61.0	128.0		1
Pr^{i}NC	*ca.* −140	**(VI)**	218.6	90.7	62.3	129.6	117.7	1
			216.4	88.4	55.5	128.9		
		(V)	219.4	86.7	61.1	127.3	118.3	1

^{a} Assignments as in structures **(V)** and **(VI)**. ^{b} Obscured by the aromatic carbon atoms of the $C_6H_3Me_2$ or Ph group.

extracted with light petroleum (b.p. 40—60 °C, 2 × 20 cm^3), reduced in volume, and passed down at 15-cm (2-cm diameter) alumina column. The first of two bands eluted with light petroleum (b.p. 40—60 °C) was unreacted [Fe(η^4-C_8H_8)(CO)$_3$] (*ca.* 10%). The second usually darker bands (elements as in Table 2) were the desired products, [Fe(η^4-C_8H_8)(CO)$_2$L], and were recrystallised from the minimum of hot light petroleum (b.p. 40—60 °C). The yields, melting points, and analyses are also included in Table 2. The ^{1}H n.m.r., ^{31}P n.m.r., infrared, and mass spectroscopic data are in Table 3.

Results and Discussion

The literature preparation[13] of [Fe(η^4-C_8H_8)(CO)$_2$(CN)]$^-$ from [Fe(η^4-C_8H_8)(CO)$_3$] and [N(SiMe$_3$)$_2$]$^-$ proved to be difficult in our hands, and so a new route was devised to synthesise [Fe(η^4-C_8H_8)(CO)$_2$L] [L = RNC or P(OMe)$_3$]. Treatment of [Fe(η^4-C_8H_8)(CO)$_3$] with Me$_3$NO[16] in the presence of a suitable ligand at room temperature gives very smoothly [Fe(η^4-C_8H_8)(CO)$_2$L] as the major product, but there was also some unreacted [Fe(η^4-C_8H_8)(CO)$_3$] and [Fe(η^4-C_8H_8)(CO)L$_2$] present. Column chromatography on alumina, followed by recrystallisation gives a pure product.

Following the arguments given in the introduction, in order to investigate the fluxionality of [Fe(η^4-C_8H_8)(CO)$_2$L] by conventional lineshape analysis techniques, it is necessary to find a compound where one isomer, **(V)** or **(VI)**, is exclusively present. Unfortunately for all the compounds synthesised the low-temperature ^{13}C n.m.r. spectra either showed the presence of a mixture, see Table 4, or in the case of L = P(OMe)$_3$, the

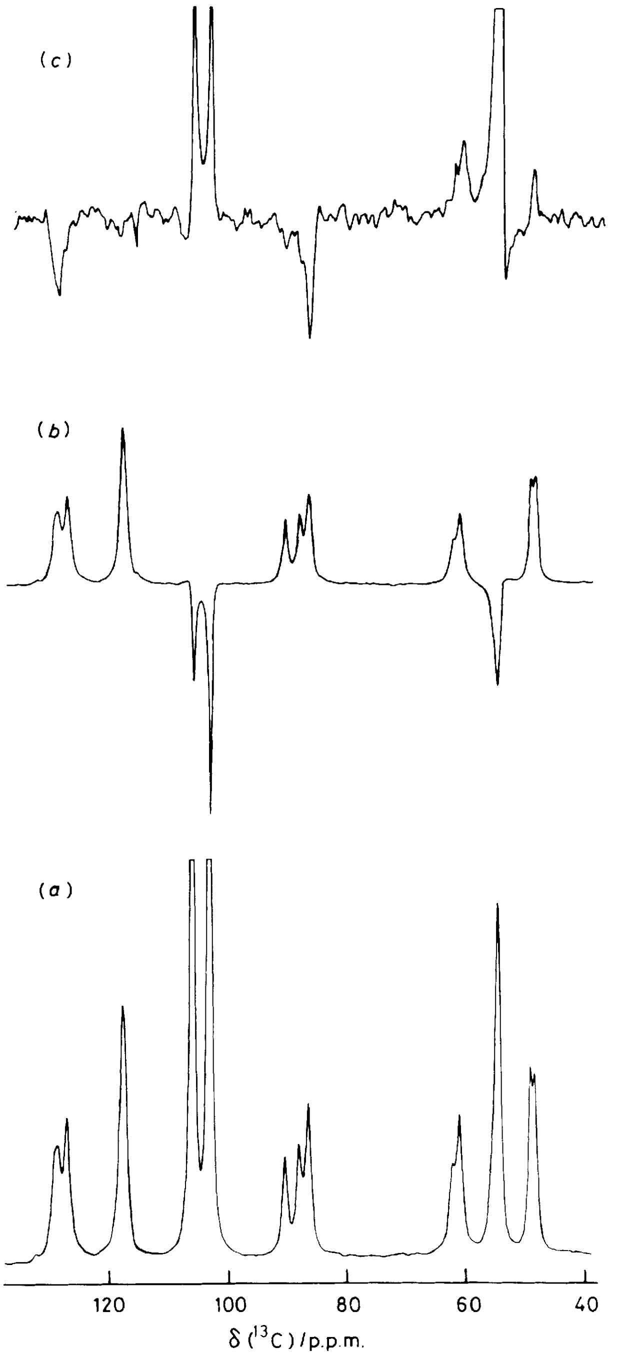


Figure. (*a*) A partial 100.6-MHz ^{13}C n.m.r. spectrum of [Fe(η^4-C_8H_8)$(CO)_2$(CNPr^i)] in CD_2Cl_2–$CHFCl_2$ (1:1) at −118 °C. In addition to the cyclo-octatetraene signals there is a doublet at δ 104.9 due to $CHFCl_2$, a weak doublet at δ 89.5 due to solvent impurity coincident with the signals due to carbons a′ and a″, a broad singlet at δ 54.6 due to CD_2Cl_2, and two signals at δ 49.2 and 48.4 p.p.m. due to the methine carbons of the ispropyl group. (*b*) The partial spectrum 1 μs after applying a selective 180° pulse at δ 55.5 p.p.m. A side-band, 5 kHz away perturbed the $CHFCl_2$ signal. (*c*) A difference spectrum obtained by subtracting spectrum (*b*) from that obtained 10 ms after applying a selective 180° pulse at δ 55.5 p.p.m.

activation energy for fluxionality is considerably lower, and a limiting low-temperature spectrum could not be obtained. Even at *ca.* −140 °C, when L = $P(OMe)_3$ the rate of leaving each carbon site in the major species (**VI**) is *ca.* 250 s^{-1} and the minor species (**V**) could have been present at a significant concentration, the signals being too broad to detect beside the sharper signals due to (**VI**). The signal assignments are in agreement with those for [Fe(η^4-C_8H_8)$(CO)_3$] and are further based on intensity and multiplicity.[3]

Magnetisation transfer measurements offer a powerful method to investigate such a complex mechanism. By applying a selective 180° pulse to one specific site, the nuclear spins in that site are specifically labelled with a non-equilibrium spin population. The Boltzmann spin population is re-established by spin–lattice relaxation, but if exchange occurs at a comparable or faster rate, then significant non-equilibrium spin population is transferred to other sites and the mechanism can be studied. This procedure has been applied recently to [$Ir_4(CO)_{11}(PEt_3)$] to demonstrate the mechanism of carbonyl exchange.[17]

[Fe(η^4-C_8H_8)$(CO)_2$(CNPr^i)] was chosen for the magnetisation transfer measurements as the ratio of isomers (**V**):(**VI**) is 1:1, so that the magnestisation transfer between the isomers can be readily detected. The DANTE pulse sequence[15] was used to apply a selective 180° pulse to the carbon b″ of (**VI**). This is the only signal which was isolated enough to excite without perturbing other cyclo-octatetraene ^{13}C signals. Due to the spread of signals over *ca.* 75 p.p.m. (7 500 Hz at 100 MHz), in order to obtain some DANTE selectivity without lengthening the subsequent observing 90° pulse beyond acceptable limits, a DANTE side-band was allowed to fall within the spectrum. The side-band fell on the $CHFCl_2$ solvent resonance, but did not perturb the cyclo-octatetraene ^{13}C signals. The normal ^{13}C spectrum is shown in the Figure (*a*) while the Figure (*b*) shows the spectrum obtained by applying a selective 180° DANTE pulse at δ 55.5 with a side-band at *ca.* 104. An observing general 90° pulse was then applied. Figure (*c*) shows the difference spectrum between that obtained with a 10-ms delay between the 180° DANTE pulse and the observing general 90° pulse and that shown in Figure (*b*). The difference spectrum shows the changes that have occurred during that 10 ms. The signal at δ 55.5 has recovered by spin–lattice relaxation and exchange while the signal at δ 104 has recovered by spin–lattice relaxation. Chemical exchange has transferred magnetisation inversion from the signal at δ 55.5 to that at δ 86.7 which is unambiguously assigned to carbon a in (**V**) and to that at δ 129 which is assigned to carbon c′ and c″ of (**VI**). This observation is completely consistent with the mechanism in Scheme 4, provided that the signal at δ 55.5 is assigned to carbon b″. The alternative assignment of this signal to carbon b′ does not produce magnetisation transfer results consistent with any suggested mechanism.

Alternative mechanisms can be eliminated. A simple slide of the metal over the cyclo-octatetraene ring would not interconvert isomers (**V**) and (**VI**) and magnetisation transfer to carbon a in (**V**) would not have occurred. A ligand scrambling at the iron would produce b′ ⟷ b″ interchange which is not observed. Attempts to devise another mechanism which is consistent with experiment have so far failed. This experiment is then a proof of the applicability of the Woodward–Hoffmann rules to the fluxionality of [Fe(η^4-C_8H_8)$(CO)_2$L].

Acknowledgements

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