Journal of Organometallic Chemistry, 266 (1984) 69–82
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE SOLUTION STRUCTURE AND FLUXIONAL BEHAVIOUR OF (η^4-ENONE)Fe(CO)$_2$L COMPLEXES (L = PHOSPHINE, PHOSPHITE)

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(Received December 19th, 1983)

Summary

(η^4-enone)Fe(CO)$_2$L complexes (enone = benzylideneacetone, cinnamaldehyde; L = $PPh_{3-x}Me_x$ (x = 0–2), $P(OPh)_3$) exist as interconverting isomeric mixtures in solution in which L occupies either the axial or basal position of a square pyramidal structure. The ratio of isomers is dependent on the steric properties of both L and the enone.

Introduction

Exchange reactions using (η^4-enone)Fe(CO)$_3$ complexes provide one convenient method for the synthesis of (η^4-diene)Fe(CO)$_3$ complexes under mild conditions, and we have recently reported a detailed kinetic study of this reaction [1]. The synthesis [2] of (η^4-enone)Fe(CO)$_2$L complexes (L = PPh_3, $P(OPh)_3$) and the demonstration of their exchange with 1,3-cyclohexadiene provides an opportunity for a kinetic study of the influence of auxiliary ligand on the rates and mechanism of this reaction. The results of this kinetic study are reported in the succeeding paper in this journal [3]. During the course of this work, however, these complexes have also revealed novel structural and fluxional features, which we wish to describe in this present article.

Intramolecular site exchange in (η^4-diene)Fe(CO)$_3$ complexes has been well investigated [4a–4g] and experiments particularly on (η^4-diene)Fe[P(OMe)$_3$]$_3$ complexes [5a–5c] have established the mechanism of exchange as either a simple diene rotation relative to ML_3 or an indistinguishable sequential Berry pseudorotation. For complexes of intermediate degrees of substitution ((diene)Fe(CO)$_x$L$_{3-x}$; x = 1,2), two isomeric forms are possible for each, as represented below on the basis of a distorted square pyramidal geometry.

The available data on complexes of these types is rather fragmentary, and is summarized in Table 1.

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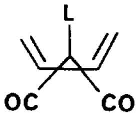
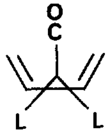
0022-328X/84/$03.00

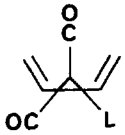
For the most complete series involving PF_3, the results indicate a preference of PF_3 for the axial position of the square pyramid, although the basal isomer is also populated through steric hindrance in cases where both terminal carbons of the



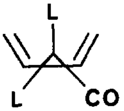
(a)
axial



(bb)
basal-basal



(b)
basal



(ab)
axial-basal

TABLE 1

ISOMERIC DISTRIBUTIONS OF REPORTED (DIENE)ML'$_x$L$_{3-x}$ (x = 1, 2)

Complex	Isomers present in solution	Major isomer	Ref.
(diene)Fe(CO)$_2$L			
diene = butadiene, 2,3-dimethylbutadiene, *trans*, *trans*-2,4-hexadiene, 2,4-dimethyl-1,3-butadiene, *cis*- and *trans*-1,3-pentadiene, isoprene; L = PF_3	**a** only	–	6a, 6b
diene = chd [a], L = PF_3	**a**, **b**	**b**	7
diene = chd, L = $P(OCH_2)_3CEt$	**b** only	–	8
diene = chd, butadiene 2,3-dimethylbutadiene; L = CNR (R = Me, EMe_3, E = Si, Ge, Sn)	**b** only	–	9a, 9b
diene = *trans*-1,3-pentadiene, L = CNR	**a**, **b**	**b**	
diene = cot [a], L = $CNPr^i$	**a**, **b**	equal	10
(diene)Fe(CO)L$_2$			
diene = butadiene, 2,3-dimethylbutadiene, *cis*- and *trans*-1,3-pentadiene, isoprene, 2,4-dimethyl-1,3-pentadiene; L = PF_3	**ab** only	–	6a, 6b
diene = chd; L = PF_3, $P(OCH_2)_3CEt$; L_2 = diphos	**ab**, **bb**	**ab**	7, 8, 11
(diene)RuL'$_2$L			
diene = butadiene; L' = $P(OMe)_3$, L = PPh_3	**a**, **b**	**a**	12

[a] chd = 1,3-cyclohexadiene, cot = 1,3,5,7-cyclooctatetraene.

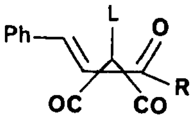
diene are alkyl substituted. However, PF_3 may represent a rather special case in its resemblance in bonding properties to CO, and both cyclic and acyclic (diene)Fe$(CO)_2$CNR complexes exist predominantly or exclusively as the basal isomer. We wish here to report on the analogous axial $\rightleftharpoons$ basal equilibria and fluxional behaviour of (η^4-enone)Fe$(CO)_2$L complexes.

Results and discussion

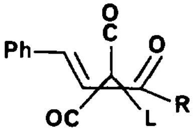
The complexes under study, (cinn)Fe$(CO)_2$L (cinn = cinnamaldehyde (*trans*-3-phenylpropenal); L = PPh_3, PPh_2Me, $PPhMe_2$) and (bda)Fe$(CO)_2$L (bda = benzylideneacetone (*trans*-4-phenyl-3-buten-2-one); L = PPh_3, PPh_2Me, $PPhMe_2$, $P(OPh)_3$), were prepared as described in the Experimental section. Infrared spectra and room temperature ^{1}H NMR spectra are given in Table 2, while variable temperature ^{31}P and ^{13}C NMR spectra are summarized in Table 3. NMR assignments are based on decoupling and variable pulse length experiments, and are unambiguous except for the ketonic carbonyl resonance of the (bda)Fe$(CO)_2$L complexes at ca. 141 ppm. Another resonance at ca. 137 ppm may also be a candidate, but this is assigned to the quaternary carbon of the phenyl ring on the basis of its similarity in chemical shift to that carbon of free benzylideneacetone (134.1 ppm).

(a) Axial $\rightleftharpoons$ basal isomer distribution

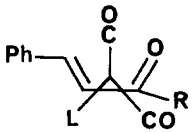
Crystal structure determinations of (cinn)Fe$(CO)_2PPh_3$ [13] and (bda)Fe$(CO)_2$L (L = PEt_3, $PPhMe_2$) [14] show that they exist in the solid state as the axially substituted isomer **A**:



(A)



(B)

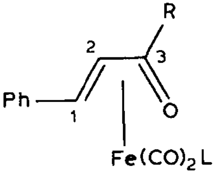
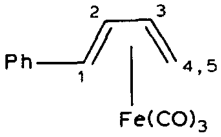


(B')

Although the room temperature ^{31}P NMR spectrum of (bda)Fe$(CO)_2PPh_3$ in toluene consists of a single resonance, cooling to −70°C yields the spectrum shown in Fig. 1(a). Experiments at intermediate temperatures show clearly that the small resonance at 55.0 ppm does exchange with the major resonance at 52.6 ppm and is not an impurity. The major resonance is thus assigned to that of the solid state isomeric structure **A**, while the minor resonance is assigned to the basal isomer **B** (rather than **B'**; vide infra); the **A**/**B** ratio determined from peak heights is 59/1. ^{13}C NMR spectra of (bda)Fe$(CO)_2PPh_3$ in dichloromethane at low temperature (Fig. 2(a)) do not show the presence of **B** due to its low abundance. Only two M–CO resonances, one which is phosphorus coupled, are observed and are assigned to the inequivalent carbonyls of structure **A**. An absolute assignment of these signals may be attempted on the basis of a correlation between (*trans*-1-phenylbutadiene)Fe$(CO)_3$, (bda)Fe$(CO)_3$ and (bda)Fe$(CO)_2PPh_3$, as shown in Scheme 1.

A comparison of the crystal structures of (η^4-butadiene)Fe$(CO)_3$ (Fe–CO(basal) 1.77 Å) and (cinn)Fe$(CO)_3$ (Fe–CO(basal) 1.76 (*trans*) and 1.80 Å (*cis*)) shows a lengthening of the Fe–CO bond *cis* to the π-bound ketonic group [22]. On the

TABLE 2. INFRARED AND ^1H NMR DATA

	Complex	$\nu(CO)$ [a]	H(1) [b]	H(2)	H(3)	other
	L = PMe_2Ph	2000(10.0) 1940(9.5)	2.40 (t) (J(1–2) 8.2, J(P–H) 8.8)	5.31 (tt) ($J(2–3) \cong J$(P–H) 1.5)	[c]	Ph 6.60–7.50 (m) P–Me 1.35 (q)
	L = $PMePh_2$	2005(10.0) 1942(9.2)	2.54 (t,br)	5.41 (tt) (J(1–2) 9.2; $J(2–3) \cong$ J(P–H) 1.3)	[c]	Ph 6.71–7.56 (m) P–Me 1.84 (d) (J(P–H) 8.5)
R = H	L = PPh_3	2000(10.0) 1939(8.8)	2.90 (d,br)	5.47 (d) (J(1–2) 8.3)	6.34(d) (J(2–3) 1.2)	Ph 6.81–7.56 (m)
R = Me	L = PMe_2Ph	1994(10.0) 1930(8.0)	2.17 (t) (J(1–2) 8.5, J(P–H) 10.0)	5.50 (dd) (J(P–H) 2.5)	–	Ph 6.96–7.56 (m) Me 2.40 (d) (J(P–H) 2.5) P–Me 1.54 (d) (J(P–H) 9.6)
	L = $PMePh_2$	1995(10.0) 1931(6.5)	2.32 (t) (J(1–2) 8.5, J(P–H) 9.9)	5.63 (dd) (J(P–H) 2.4)	– –	Ph 6.90–7.78 (m) Me 2.48 (d) (J(P–H) 2.8) P–Me 1.91 (d) (J(P–H) 7.9)
	L = PPh_3	2000(10.0) 1942(8.5)	2.20 (t)	5.46 (dd) (J(1–2) 8.8, J(P–H) 2.1)	–	Me 2.20 (d) (J(P–H) 2.2) Ph 6.7–7.5 (m)
	L = $P(OPh)_3$	2014(10.0) 1961(9.5)	3.29 (t) (J(1–2) 8.8, J(P–H) 10.7)	5.61 (dd) (J(P–H) 2.6)		Ph 6.97–7.49 (m) Me 2.31 (d) (J(P–H) 4.8)
		2042 1992 1983	2.07 (m)	5.93 (m)	5.41 (m)	H(4) 0.66 (m) H(5) 1.90 (m) Ph 7.25 (m)

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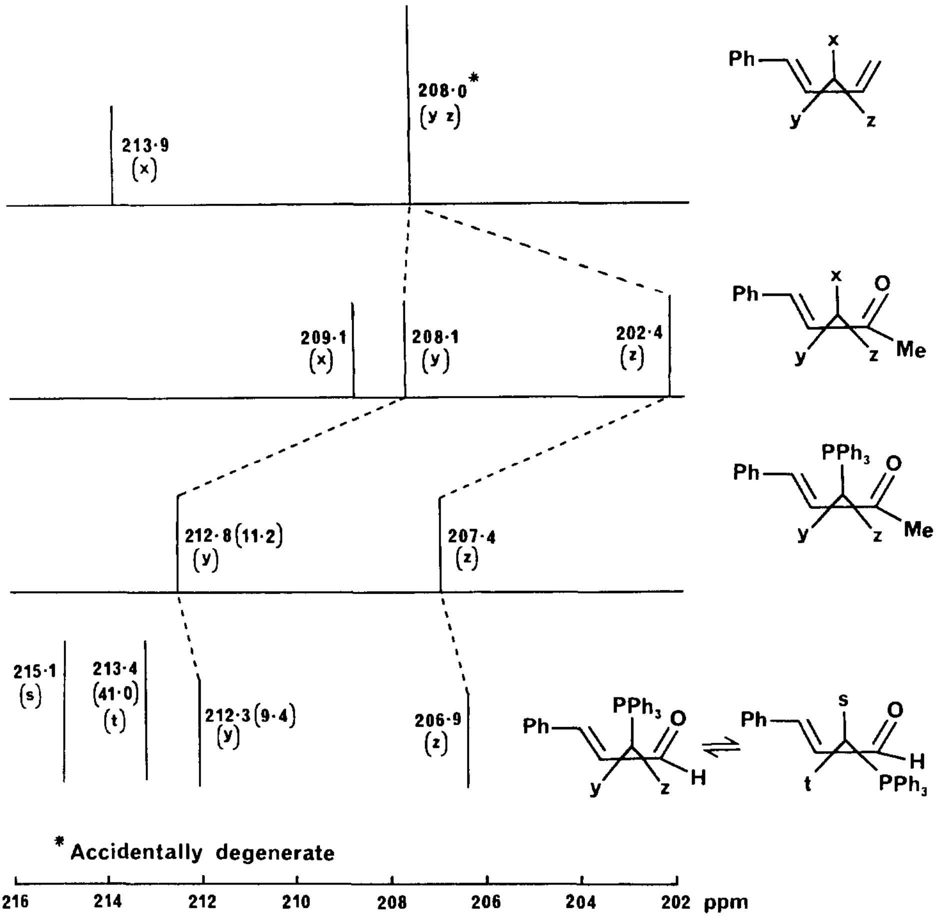
[a] Heptane solution, room temperature, cm^{-1}. [b] Benzene-d_6 solution, room temperature, ppm from TMS, J in Hz; d = doublet, t = triplet, dd = doublet of doublets, tt = triplet of triplets, q = quartet, m = multiplet, br = broadened. [c] Under phenyl resonance.



SCHEME 1

assumption that this reflects a decreased π-back donation, the resonances of (bda)Fe(CO)$_3$ are assigned as shown in Scheme 1. Crystal structure determinations of (cinn)Fe(CO)$_2$PPh$_3$ and (bda)Fe(CO)$_2$L (L = PPhMe$_2$, PEt$_3$) also show the ordering Fe–CO(*cis*) > Fe–CO(*trans*), although both are shortened relative to (cinn)Fe(CO)$_3$ because of increased back donation [13,14]. Thus, the downfield shift of both resonances for (bda)Fe(CO)$_2$PPh$_3$, as shown in Scheme 1, is expected.

The ^{31}P and ^{13}C NMR spectra of (bda)Fe(CO)$_2$PPh$_2$Me and (bda)Fe(CO)$_2$P-PhMe$_2$ exhibit similar features (Table 3). The ^{31}P NMR spectrum of (bda)Fe(CO)$_2$P(OPh)$_3$ at low temperature also reveals two resonances, but with the major resonance now at the highest chemical shift. However, the essential similarity of the ^{13}C NMR spectrum to those of the other bda complexes indicates that **A** is still the major isomer, and that the ordering of axial versus basal phosphorus chemical shifts has been reversed for P(OPh)$_3$. The isomeric ratio **A**/**B** may be seen to increase in the order P(OPh)$_3$ < PPh$_3$ < PPhMe$_2$.

^{31}P NMR spectra of (cinn)Fe(CO)$_2$PPh$_3$ are also temperature dependent (Fig. 1b–1d), showing, at −50°C, two resonances at 52.3 and 56.8 ppm which broaden

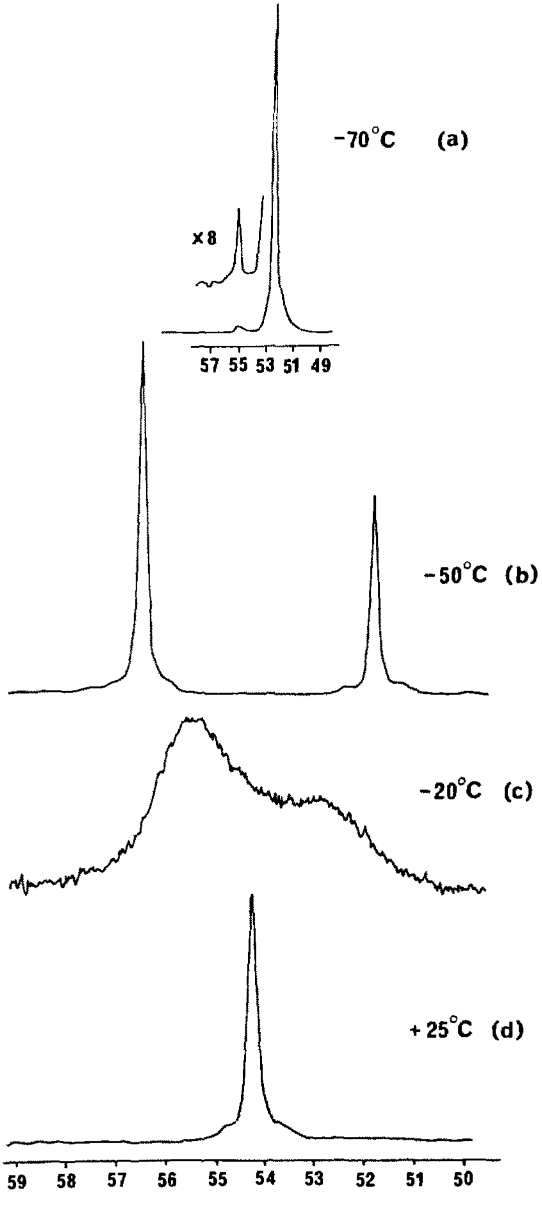


Fig. 1. ^{31}P NMR spectra of (a) (bda)Fe(CO)$_2$PPh$_3$ (in toluene), (b)–(d) (cinn)Fe(CO)$_2$PPh$_3$ (in dichloromethane).

and coalesce to a single resonsance at +25°C. By analogy with (bda)Fe(CO)$_2$PPh$_3$, these resonances are assigned to isomers **A** and **B** respectively. The relative intensities show a substantial change compared to (bda)Fe(CO)$_2$PPh$_3$, with the basal isomer **B** now being the major isomer in solution (**A**/**B** ratio 0.60/1). Low temperature ^{13}C NMR spectra are in agreement (Fig. 2b–2d); M–CO resonances due to the minor isomer **A** at 206.9 and 212.3 ppm (J(P–C) 9.4 Hz) may be assigned as shown

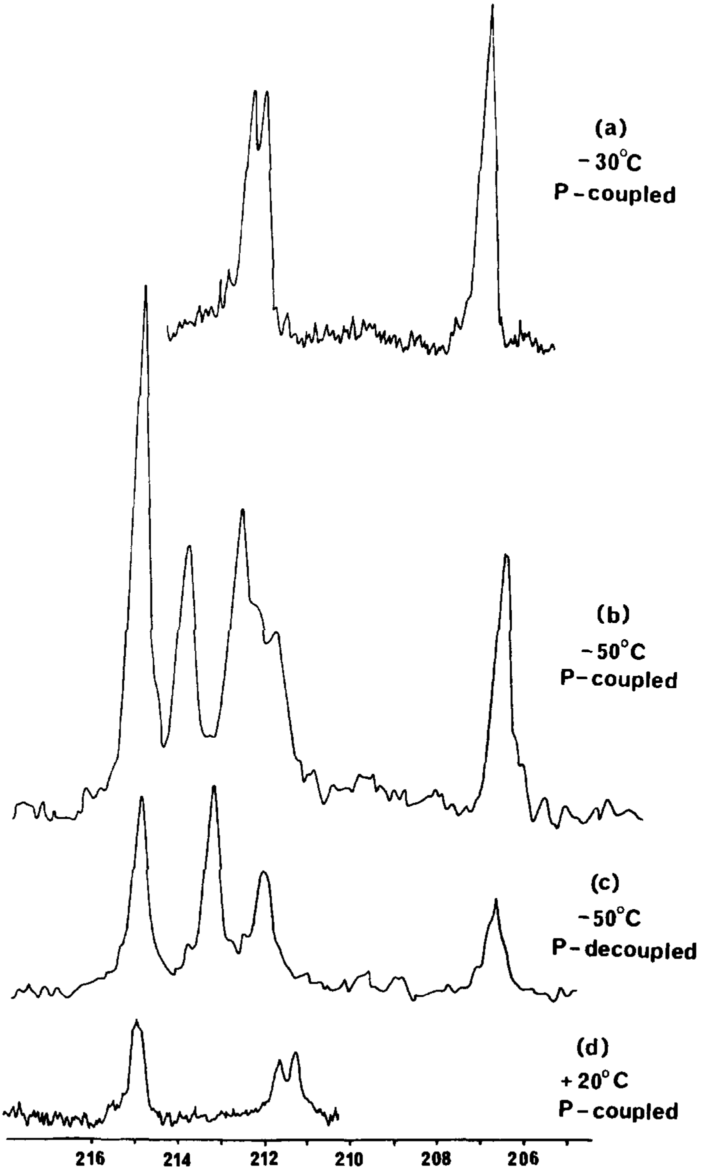


Fig. 2. ^{13}C NMR spectra of (a) (bda)Fe$(CO)_2PPh_3$ and (b)–(d) (cinn)Fe$(CO)_2PPh_3$ (in dichloromethane).

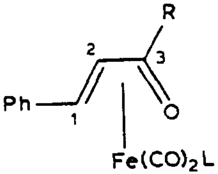
in Scheme 1 on the basis of their similarity to the resonances of (bda)Fe$(CO)_2PPh_3$, while resonances due to the major isomer **B** are observed at 215.1 and 213.4 ppm (J(P–C) 41.0 Hz). The assignment of the resonances of **B**, as shown in Scheme 1, is discussed in section (b).

Spectra of (cinn)Fe$(CO)_2L$ (L = PPh_2Me, $PPhMe_2$) may be assigned similarly (Table 3). In all cases except (bda)Fe$(CO)_2P(OPh)_3$, the ordering of the ^{31}P chemical shifts assigned to **A** and **B** is **B** > **A**, and it is worth noting that this is opposite to the

(Continued on p. 78)

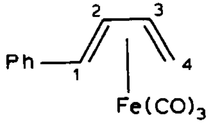
TABLE 3

^{13}C [a] AND ^{31}P [b] NMR DATA [c]



R = H

Complex	*T* (°C)	C(1)	C(2)	C(3)	CO	other	^{31}P	Ratio of **A/B**
L = CO	−40	63.2	82.8	122.2	202.1			
					207.5			
					209.2			
	+25				206.6 (br)	Ph 128.6–137.8		
L = PMe_2Ph [d]	−60	59.2	81.9 [f]	117.0	207.3 *		27.1*	2.85/1
		[e]		117.8*	213.2 (13.6)		31.9	
					213.9 (33.2)			
					215.3			
	+25				209.3 (br)	Ph 124.5–140.5		
					213.6 (9.8)	P–Me 16.1 (29.3)		
						14.5 (29.3)		
L = $PMePh_2$ [d]	−50	62.2	81.8	118.4*	206.3 *		36.1*	2.70/1
		[e]	81.3*	118.7	212.0 (13.6)		48.0	
					212.6 (31.3)			
					214.3			
	+25				208.7 (11.7)	Ph 125.0–140.6		
					212.9 (7.9)	P–Me 14.9 (27.9)		
L = PPh_3 [d]	−50	64.9	81.7*	117.6	206.9		52.3	
		[e]	83.2	120.0*	212.3 (9.4)		56.8*	0.60/1
					213.4 (41.0) *			
					215.1			
	+25				211.6 (20.2)	Ph 125.3–140.4		
					215.0 (br)			
	−50 [g]						51.8*	2.16/1
							54.8	
	−50 [h]						50.8	0.55/1
							55.2*	

R = Me	L = CO	−40	60.3	77.7	140.4	202.4 208.1 209.1	Ph 128.6–136.6 Me 20.2		
		+25				208.2 (br)			
	L = PMe$_2$Ph[i]	+25	58.6	78.9	141.6	207.9 214.0 (13.6)	Ph 124.7–138.0 Me 21.4 P–Me 16.8 (27.3) 14.6 (27. 3)	25.2	
		−70						25.8* 33.5	86/1
	L = PMePh$_2$[i]	+25	60.1	79.6	141.1	207.6 213.1 (11.7)	Ph 124.8–137.5 Me 21.5 P–Me 14.6 (29.4)	38.9	
	L = PPh$_3$[i]	25	62.8	79.4	140.3	207.4 212.8 (11.2)	Ph 124.0–136.4 Me 20.7	52.3	
		−70						52.6* 55.0	59/1
	L = P(OPh)$_3$[i]	+25	59.1	78.2	140.3	205.9 210.4 (16.2)	Ph 121.0–129.3, 151.0 Me 20.9	167.6	
		−60						162.7 170.3*	21/1
		−80	59.4	82.1	81.2	207.8 214.0	Ph 126–129 C(4) 38.8		

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[a] ppm from TMS, proton decoupled, J(P–C) values in Hz in parentheses. [b] ppm from 85% H_3PO_4, proton decoupled. [c] Solutions in CH_2Cl_2/CD_2Cl_2 unless otherwise noted. [d] Pairs of resonances due to **A**/**B** mixture; major resonance is asterisked. [e] Other resonance under solvent, but can be seen at 55.2 ppm in $CDCl_3$. [f] Only one resonance observed. [g] Toluene-d_8 solution. [h] Acetone-d_6 solution. [i] ^{13}C spectra in CH_2Cl_2/CD_2Cl_2; ^{31}P spectra in toluene-d_8.

ordering (**A** > **B**) reported in the literature [5–8] for (diene)Fe(CO)$_x$L$_{3-x}$ complexes. The ordering of the observed P–C coupling constants does, however, indicate the correctness of our assignments. Thus, it has been shown that in (butadiene)-Ru[P(OMe)$_3$]$_2$PPh$_3$, which exists as two isomers with PPh$_3$ in axial and basal positions, J(P(OMe)$_3$(basal)–PPh$_3$(basal)) > J(P(OMe)$_3$(axial)–PPh$_3$(basal)) [12]. Similarly, in the two CO resonances of **A** and **B** which show P–C coupling (Fig. 2), we find that J(PPh$_3$(basal)–CO(basal)) (41.0 Hz; isomer **B**) > J(PPh$_3$-(axial)–CO(basal)) (9.4 Hz; isomer **A**).

The **A**/**B** ratio for the (cinn)Fe(CO)$_2$L complexes may be determined from peak heights in the low temperature ^{31}P NMR spectra, and is in the order PPh$_3$ (0.60) < PPh$_2$Me (2.70) ≤ PPhMe$_2$ (2.85). As spectroscopic data, particularly infrared frequencies and ^{13}C chemical shifts of the bound carbons, indicate no significant variation in electronic ground state structure with L, it seems most reasonable to associate the change in **A**/**B** ratio with steric effects. The decreasing **A**/**B** ratio with increasing cone angle of L (PPhMe$_2$ (122°) < PPh$_2$Me (136°) < PPh$_3$ (145°)) indicates that, at least for (cinn)Fe(CO)$_2$L complexes, the axial site of the square pyramid is the site of greatest steric hindrance. The relationship between the **A**/**B** ratio and cone angle is not linear, however, with the greatest difference being observed between PPh$_3$ and PPh$_2$Me. This is consistent with crystallographic observations [15] on *cis*-Mo(CO)$_4$L$_2$ complexes (L = PPh$_x$Me$_{3-x}$; $x = 1$–3) which show that PPh$_2$Me and PPhMe$_2$ are much more able to orient themselves to minimize steric repulsions than is PPh$_3$. An electronic effect on the **A**/**B** ratio seems apparent in the (bda)Fe(CO)$_2$L series, where the population of the basal isomer for L = P(OPh)$_3$ is greater than that expected simply on the basis of cone angle (128°). Infrared spectra in particular indicate significantly less M–CO back donation in the P(OPh)$_3$ complex, consistent with the decreased σ/π ratio of P(OPh)$_3$ as compared to PPh$_x$Me$_{3-x}$. The results indicate a preference of the better π-accepting P(OPh)$_3$ for the basal position of the square pyramid. Theoretical calculations [16] show that axial-basal site preference depends on the degree of pyramidality (i.e., the L$_{\text{axial}}$–M–L$_{\text{basal}}$ angle θ); if $\theta > 100°$, the axial position is preferred by a π-accepting ligand, whereas if $\theta < 100°$, the basal position is preferred. The averaged value of θ for (cinn)Fe(CO)$_2$PPh$_3$ is 99° [13], thus placing it very close to the borderline.

The most dramatic change in isomer population is observed on alkyl substitution of the organic carbonyl, with the **A**/**B** ratio changing in the order (bda)Fe(CO)$_2$PPh$_3$ (59/1) ≫ (cinn)Fe(CO)$_2$PPh$_3$ (0.60/1). Electronically, differences in chemical shift observed on coordination ($\Delta\delta$) indicate a significant difference in the bonding of the π-enone in (cinn)Fe(CO)$_2$PPh$_3$ (isomer **A**) as opposed to (bda)Fe(CO)$_2$PPh$_3$. Thus, in (cinn)Fe(CO)$_2$PPh$_3$, resonances due to C(1) and C(3) are shifted upfield relative to the free ligand [17] by 87.6 and 75.9 ppm respectively, whereas the analogous values for C(1) and C(3) of (bda)Fe(CO)$_2$PPh$_3$ are 80.3 and 57.3 ppm. This indicates a significantly greater back-donation to cinnamaldehyde; however, since similar differences in $\Delta\delta$ are observed in a comparison of (cinn)Fe(CO)$_3$ and (bda)Fe(CO)$_3$, and since the **A** and **B** isomers of (cinn)Fe(CO)$_2$L complexes show only slightly different chemical shifts for the π-enone carbons, the observed depopulation of the basal isomer **B** seems best ascribed to an increased steric interaction of the basal phosphine with the methyl substituent of the coordinated benzylideneacetone.

Finally, one may note that the isomeric ratio is solvent dependent. For (cinn)Fe(CO)$_2$PPh$_3$, the decrease in the **A**/**B** ratio in the order toluene (2.16) >

dichloromethane (0.60) ≈ acetone (0.55) shows a decreasing population of the axial isomer with increasing solvent polarity.

(b) Mechanism and activation energy for isomer exchange

A ⇌ **B** exchange may be interpreted using the accepted mechanism of fluxionality for (diene)$Fe(CO)_3$ complexes (Scheme 2) based on a rotation of the bound enone relative to the $Fe(CO)_2L$ fragment.

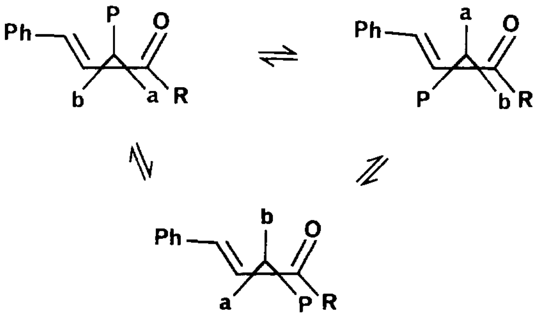
Alternatively, each 120° diene rotation can be presented as an indistinguishable sequence of two Berry pseudorotations.

Low temperature ^{31}P NMR spectra show clearly the presence of only two isomers (one of which is unambiguously **A**), and variable temperature ^{13}C NMR spectra provide justification for the assignment of the second isomer as **B** rather than **B′**. Examination of the spectra shown in Fig. 2 shows that two possibilities involving coalescence of the four low temperature resonances to the two room temperature resonances must be considered:

(i) (206.9 ↔ 213.4) and (212.3 ↔ 215.1) exchange. Based on the **A**/**B** ratio of 0.60/1 determined from the ^{31}P NMR spectrum at the same temperature, and using the coupling constants given in Table 3, predicted averaged resonances in the high temperature limiting spectrum would be expected at 211.0 (J(P–C) 25.6 Hz) and 214.0 (J(P–C) 3.5 Hz) ppm.

and (ii) (206.9 ↔ 215.1) and (212.3 ↔ 213.4) exchange. On the same basis, averaged resonances would be expected at 212.0 (J(P–C) 0 Hz) and 213.0 (J(P–C) 29.1 Hz) ppm.

Averaged resonances at +25°C are in fact found at 211.6 (J(P–C) 20.2 Hz) and 215.0 ppm, the latter being slightly broadened. Taking into account the slight temperature dependence of the chemical shifts, the possibility of a change in isomer distribution with temperature, and the fact that the high temperature limiting spectrum is not quite reached at +25°C, the results (particularly the coupling constant data) show clearly that alternative (i) is correct. Similar calculations on (cinn)$Fe(CO)_2PPh_2Me$ and (cinn)$Fe(CO)_2PPhMe_2$ are in even closer agreement. It may be noted that Scheme 2 does not provide a mechanism for total carbonyl scrambling, and indeed, ^{13}C NMR spectra in toluene of both (bda)$Fe(CO)_2PPh_3$ and (cinn)$Fe(CO)_2PPh_3$ retain two M–CO resonances up temperatures at which decomposition becomes significant (ca. +80°C).



SCHEME 2

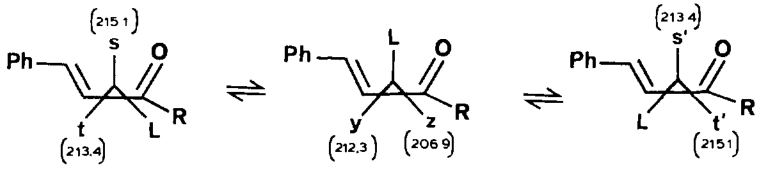
A more detailed outline of the exchange process is shown in Scheme 3.

Examination of Scheme 2 shows that if $\mathbf{A} \rightleftharpoons \mathbf{B}$ exchange is occuring, this requires coalescence of the $(y \leftrightarrow s)$ and $(z \leftrightarrow t)$ resonances of Scheme 3, whereas if $\mathbf{A} \rightleftharpoons \mathbf{B}'$ exchange is occurring, $(y \leftrightarrow t')$ and $(z \leftrightarrow s')$ coalescence is required. Using the assignment of the resonances of **A** given in Scheme 1, and knowing which resonances coalesce experimentally, assignments to (s,t) and (s',t') follow, as shown in Scheme 3. While **B** shows the accepted ordering of axial-basal carbonyl chemical shifts (axial > basal), the ordering for **B′** is the reverse of the accepted order. Further support for an assignment to **B** rather than **B′** comes from the literature, which shows that $(MeCH{=}CHCH{=}CH_2)Fe(CO)(PF_3)_2$ exists predominantly as an axial-basal isomer in which the basal PF_3 is *trans* to the methyl substituted terminal diene carbon [6a].

One caveat may be noted, in that the above discussion is based on a correct assignment of the resonances of **A** outlined in Scheme 1. If these assignments are reversed, a necessary consequence is that **B′** becomes the favoured choice for the second isomer.

Activation energies for $\mathbf{A} \rightleftharpoons \mathbf{B}$ exchange in the $(cinn)Fe(CO)_2L$ complexes are most easily calculated using coalescence temperatures of the ^{31}P NMR spectra [18]. The ΔG^* values obtained (48 ± 1 kJ mol^{-1}, $L = PPh_3$; 50 ± 1 kJ mol^{-1}, $L = PPh_2Me$; 50 ± 2 kJ mol^{-1}, $L = PPhMe_2$) show no significant variation between phosphines, but are significantly lower than the value of 58 kJ mol^{-1} reported for site exchange in $(cinn)Fe(CO)_3$ [4c,4f], a value which our results confirm [19]. The results thus indicate a lower barrier to rotation on substitution of CO by a ligand which is a better σ-donor. Such an increase in the rate of exchange with increasing CO substitution has also been observed in the $(butadiene)Fe(CO)_x(PF_3)_{3-x}$ series ($x = 0$–3) [6,7]. Similarly, although a limiting low temperature spectrum may be obtained at −100°C for $(cyclohexadiene)Fe(CO)_3$, only one sharp, phosphorus coupled resonance is observed for $(cyclohexadiene)Fe(CO)_2PPh_3$ down to −70°C, even though the solid state structure is one with non-equivalent CO ligands [20]. In contrast, however, a theoretical study [21] of diene rotation predicts an increasing barrier to rotation on substitution of CO by better σ-donors. While the barrier is also shown to depend on molecular geometry (primarily the diene–M–L angle), there is little indication of any significant difference in these variables in the solid state structures of $(cinn)Fe(CO)_3$ [22] and $(cinn)Fe(CO)_2PPh_3$ [13].

Finally, it may be noted that the barrier to rotation in $(cinn)Fe(CO)_3$ is substantially higher than that for $(butadiene)Fe(CO)_3$ (44 kJ mol^{-1}) [4c], an observation which has been attributed to the better π-accepting properties of the enone ligand.



SCHEME 3

Experimental

Infrared and NMR spectra were obtained on Pye Unicam SP 2000 and JEOL FX-100 instruments respectively; ^{13}C NMR spectra in the M–CO region were run in the presence of $Cr(acac)_3$ as relaxation agent.

$(bda)Fe(CO)_3$ [23] and $(cinn)Fe(CO)_3$ [24] were prepared by literature methods; $(cinn)Fe(CO)_2L$ and $(bda)Fe(CO)_2L$ complexes ($L = PPh_3$, PPh_2Me, $PPhMe_2$) were prepared by photolysis of $Fe(CO)_4L$ [25] in the presence of cinn or bda [2,14]. $(bda)Fe(CO)_2P(OPh)_3$ was prepared by thermal reaction of $(bda)Fe(CO)_3$ with $P(OPh)_3$ [2]. Analytically pure samples were obtained by crystallization from 40–60 petroleum ether. (*Trans*-1-phenylbutadiene)$Fe(CO)_3$ was prepared by a literature method [26] and purified by sublimation.

Microanalytical and m.p. data for new complexes are given below:

$(cinn)Fe(CO)_2L$	M.p. (°C)	Found (calcd.) (%))	
		C	H
$L = PPh_2Me$	105	65.2 (64.9)	4.33 (4.77)
$L = PPhMe_2$	71	60.1 (60.3)	5.11 (5.07)

Acknowledgment

We thank the Association of Commonwealth Universities for the award of a Commonwealth Scholarship (J.K.).

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17 Chemical shifts for C(1) to C(3) of cinnamaldehyde are 152.5, 128.2 and 193.5 ppm and for benzylideneacetone are 143.1, 127.2 and 197.6 ppm respectively. C(2) shifts upfield by approximately the same amount in both (cinn)$Fe(CO)_2PPh_3$ (45.1 ppm) and (bda)$Fe(CO)_2PPh_3$ (47.4 ppm).
18 ^{31}P coalescence temperatures (T_c) for (cinn)$Fe(CO)_2L$ complexes are 255 K (PPh_3), 273 K (PPh_2Me) and 263 K ($PPhMe_2$). $\Delta G^\star$ values were calculated using the equation $\Delta G^\star = 2.303RT_c\log\sqrt{2}\,kT_c/\pi h\Delta w$ kJ mol^{-1}, where Δw is the chemical shift difference in Hz between the low temperature limiting resonances. Note that this expression is only strictly accurate for equally populated sites.
19 From the coalescence of the two low field CO signals (207.5, 209.5 ppm; Table 3), at 275 K, a $\Delta G^\star$ value of 57 ± 3 kJ mol^{-1} may be calculated.
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