Journal of Organometallic Chemistry, 266 (1984) 83–96
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE KINETICS AND MECHANISM OF DIENE EXCHANGE IN (η^4-ENONE)$Fe(CO)_2L$ COMPLEXES (L = PHOSPHINE, PHOSPHITE)

JAMES A.S. HOWELL *, JOHN C. KOLA, DENIS T. DIXON, PHILIP M. BURKINSHAW and MARION J. THOMAS

Chemistry Department, University of Keele, Keele, Staffordshire ST5 5BG (Great Britain)

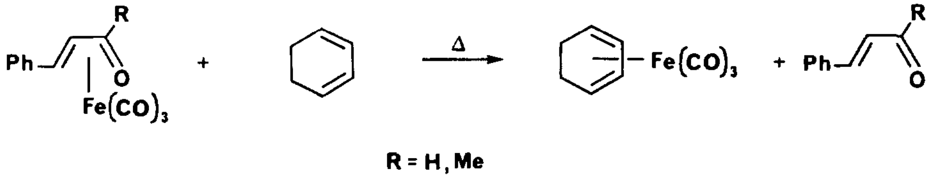
(Received December 19th, 1983)

Summary

Kinetic data for the exchange of 1,3-cyclohexadiene with (η^4-benzylideneacetone)$Fe(CO)_2L$ complexes (L = CO, $PPh_{3-x}Me_x$ ($x = 0$–2) or $P(OPh)_3$) to give (η^4-1,3-cyclohexadiene)$Fe(CO)_2L$ derivatives indicate a mechanism involving stepwise competing D and I_d opening of the ketonic M–CO π-bond. Rates increase in the order $CO \gg PPh_3 \approx P(OPh)_3 > PPh_2Me \gg PPhMe_2$, and both steric and electronic factors appear to be important. (η^4-1,3-cyclohexadiene)$Fe(CO)_2L$ complexes of potential use in enantioselective synthesis (L = (+)-Ph_2P(menthyl) or (+)-$Ph_2PCH_2CH(Me)Et$) may be prepared via their (η^4-benzylideneacetone)$Fe(CO)_2L$ complexes.

Introduction

One of the notable successes in the organometallic chemistry of iron is the utility of tricarbonyliron complexes in organic synthesis [1a–1c]. Not only does the tricarbonyliron moiety function as a protecting group, but it also promotes high stereo- and regiospecificity in reactions of its complexes. One primary difficulty has been the high temperatures and the resultant mixtures formed in the synthesis of (η^4-diene)$Fe(CO)_3$ complexes from $Fe(CO)_5$. One alternative method which has received some attention is the exchange reaction under mild conditions of more labile (η^4-enone)$Fe(CO)_3$ complexes



---

* To whom correspondence should be addressed.

0022-328X/84/$03.00 © 1984 Elsevier Sequoia S.A.

developed initially by Lewis and coworkers [2], and later workers have demonstrated particularly the marked selectivity of this reaction in the trapping of tautomeric polyenes [3a–3d]. We [4a,4b] and others [3c] have investigated this reaction kinetically and found that the results are most consistent with a stepwise exchange in which the rate-determining step involves competing *D* and I_d opening of the ketonic M–CO bond *.

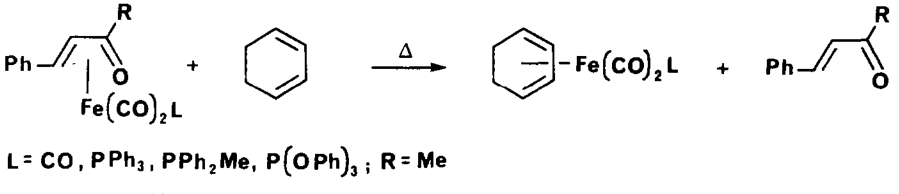
Recently, related (η^4-enone)Fe(CO)$_2$L complexes (L = PPh$_3$, P(OPh)$_3$) have been synthesized and shown to undergo exchange with 1,3-cyclohexadiene (chd) to give (chd)Fe(CO)$_2$L complexes in good yields [5]. From a kinetic point of view, this provides an ideal opportunity for the study of the influence of auxiliary ligand on the rates and mechanism of this reaction. From a synthetic point of view, this reaction may prove valuable in producing useful (diene)Fe(CO)$_2$L complexes and, inter alia, [(η^5-dienyl)Fe(CO)$_2$L]X salts. The little that is known shows that the reactivity of such derivatives can be significantly different from that of their tricarbonyl analogues. Thus, acetylation of (chd)Fe(CO)$_2$PPh$_3$ proceeds in better yield than that of (chd)Fe(CO)$_3$ [6], while the observed position of nucleophilic attack on [(η^5-cycloheptadienyl)Fe(CO)$_2$PPh$_3$]$^+$ is modified relative to that of its tricarbonyl analogue [7a, 7b].

The results of these kinetic studies are reported in this article, together with some synthetic results of relevance in the possible use of these complexes in enantioselective synthesis. During the course of this work, these (η^4-enone)Fe(CO)$_2$L complexes have also revealed interesting structural and fluxional properties which are described in the preceding paper in this journal [8].

Results and discussion

(a) Kinetics

The reactions shown below were examined kinetically in toluene (L = CO), in 100–120 petroleum ether (L = CO, PPh$_3$, P(OPh)$_3$), or 120–160 petroleum ether (L = PPh$_2$Me) at the temperatures given in Table 1. The substrate complexes (η^4-bda)Fe(CO)$_3$, (η^4-bda)Fe(CO)$_2$L (bda = benzylideneacetone (*trans*-4-phenyl-3-buten-2-one), L = PPh$_3$, PPh$_2$Me, PPhMe$_2$, P(OPh)$_3$) and (η^4-cinn)Fe(CO)$_2$PPh$_3$ (cinn = cinnamaldehyde (*trans*-3-phenylpropenal)) were prepared as described [8]. The product (chd)Fe(CO)$_2$L complexes (L = PPh$_3$, PPh$_2$Me, P(OPh)$_3$ were prepared on a synthetic scale and characterized by microanalysis and spectroscopy (see Experimental section).



L = CO, PPh$_3$, PPh$_2$Me, P(OPh)$_3$; R = Me

L = PPh$_3$; R = H

The reactions were conveniently monitored by infrared spectroscopy using the method described in the Experimental section; although all product and substrate

---

* *D* and I_d mean dissociative and interchange dissociative, respectively. For an explanation, see J.A.S. Howell and P.M. Burkinshaw, Chem. Reviews, 83 (1983) 557.

TABLE 1

OBSERVED RATE CONSTANTS FOR REACTION OF (bda)Fe(CO)$_2$L COMPLEXES WITH 1,3-CYCLOHEXADIENE

L	Solvent	Temp. (°C)	[chd] (mol dm^{-3})	10^4k_{obs} (s^{-1})	
CO	toluene[a]	70.2	0.049	10.9	11.2
			0.098	14.8	15.2
			0.196	20.7	19.7
			0.392	23.6	24.0
			0.539	25.5	25.5
			0.637	25.0	25.6
			0.735	25.9	25.7
			0.882	26.4	26.9
CO	100–120 petroleum ether[b]	70.4	0.025	10.5	11.0
			0.049	13.0	12.7
			0.098	17.4	17.7
			0.196	23.2	22.6
			0.270	25.2	26.4
			0.319	26.6	26.0
			0.368	26.6	27.5
			0.441	28.2	28.7
PPh_3	100–120 petroleum ether[b]	70.1	0.058	0.34	0.34
			0.116	0.39	0.39
			0.173	0.46	0.44
			0.231	0.43	0.46
			0.289	0.46	0.47
$P(OPh)_3$	100–120 petroleum ether[b]	70.1	0.025	0.24	0.24
			0.049	0.31	0.34
			0.098	0.40	0.38
			0.147	0.41	0.43
			0.245	0.43	0.44
			0.294	0.48	0.46
			0.343	0.48	0.48
PPh_2Me	120–160 petroleum ether[b]	91.2	0.025	0.16	0.16
			0.049	0.20	0.20
			0.098	0.26	0.26
			0.147	0.29	0.28
			0.196	0.31	0.30
			0.245	0.34	0.36
			0.294	0.38	0.38

[a] [(bda)Fe(CO)$_3$] 4.9×10^{-3} mol dm^{-3}. [b] [(bda)Fe(CO)$_2$L] 2.45×10^{-3} mol dm^{-3}.

absorptions are well separated, k_{obs} values were determined by monitoring of the disappearance of the highest frequency CO absorption of the (bda)Fe(CO)$_2$L complexes (L = CO, 2065 cm^{-1}; L = PPh$_3$, 2000 cm^{-1}; L = PPh$_2$Me, 1995 cm^{-1}; L = P(OPh)$_3$, 2014 cm^{-1}). Values of k_{obs} are tabulated in Table 1, while plots of k_{obs} against [chd] are shown in Figs. 1 and 2.

Although exchange using (bda)Fe(CO)$_3$ is quantitative, reactions using the phosphine and phosphite derivatives are not quite so. Infrared calibration at the end of the reaction using solutions of known concentration shows that in addition to (chd)Fe(CO)$_2$PPh$_3$ (91% yield), (chd)Fe(CO)$_3$ (4%) is also formed. The remaining 5% is attributed to the formation of decomposition products which appear as a brown film on the walls of the reaction vessel. Essentially similar figures are observed for (bda)Fe$(CO)_2$P$(OPh)_3$; for (bda)Fe$(CO)_2$$PPh_2$Me, which was studied at higher temperature, an 86% yield of (chd)Fe$(CO)_2$$PPh_2$Me and a 9% yield of (chd)Fe$(CO)_3$ are observed. In no reaction are infrared bands attributable to any intermediate observed.

Within the limits of reproducibility of the experiments, the ratio of (chd)Fe$(CO)_2$$PPh_3$ to (chd)Fe$(CO)_3$ is independent of the concentration of chd used. Although this ratio can provide information relevant to the mechanism, its insensitivity (at least in the absence of added CO) to changes in the amount of (chd)Fe$(CO)_3$ produced, together with the need for measurement at completion of reaction (thus reflecting any differential rate of decomposition of (chd)Fe$(CO)_2$$PPh_3$ and (chd)Fe$(CO)_3$) limits its value in the present case.

The following observations are also relevant to the mechanistic discussion presented in section (b):

(i) In the absence of chd, (bda)Fe$(CO)_2$$PPh_3$ (2.45×10^{-3} mol dm^{-3}) slowly decomposes thermally at 70°C in 100–120 petroleum ether ($t_{1/2} \approx 3$ d) to give a 30% yield of (bda)Fe$(CO)_3$. This may be compared with the half-life for the slowest exchange reaction of this complex of about 6 h.

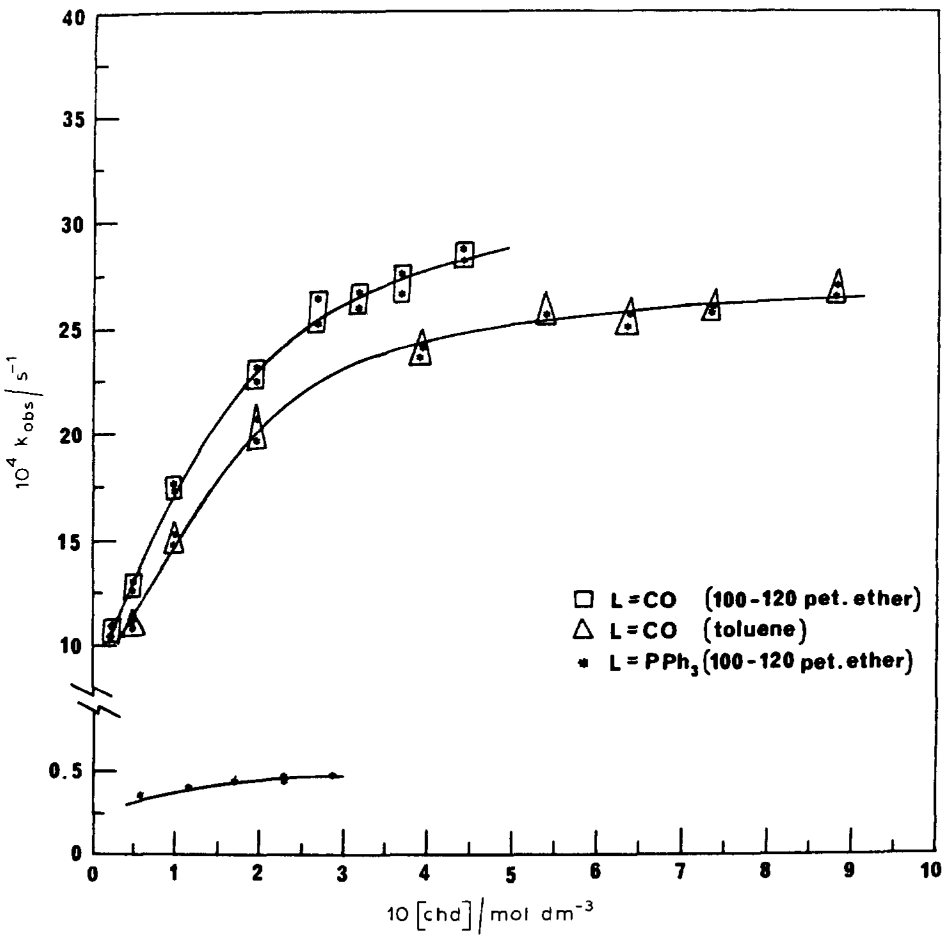


Fig. 1. Plot of k_{obs} against [chd] for reaction of (bda)Fe$(CO)_2$L with chd (L = CO, PPh_3).

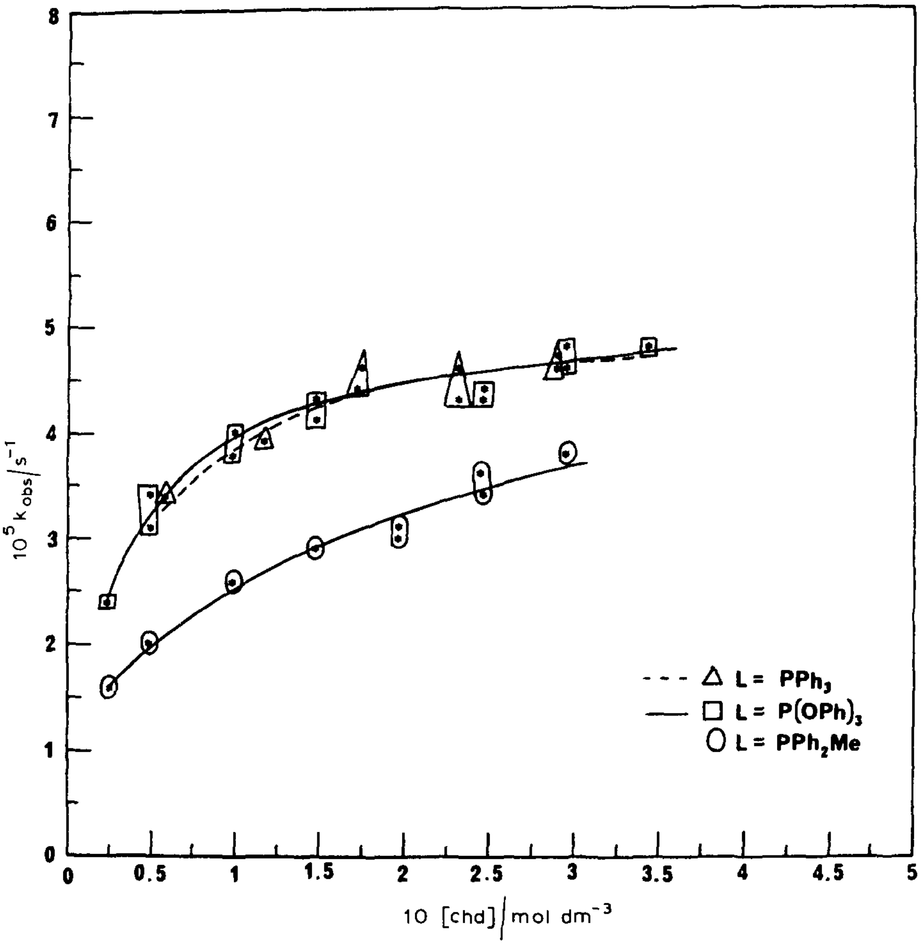


Fig. 2. Plot of k_{obs} against [chd] for reactions of (bda)Fe(CO)$_2$L with chd (L = PPh$_3$, P(OPh)$_3$, PPh$_2$Me).

Under one atmosphere of CO and in the absence of chd, thermolysis provides an 80% yield of (bda)Fe(CO)$_3$, with the rate of disappearance of substrate being much faster than the value obtained in the absence of CO. No infrared detectable quantities of Fe(CO)$_4$PPh$_3$ or Fe(CO)$_5$ are formed.

The PPh$_2$Me and P(OPh)$_3$ complexes decompose in a similar fashion at the temperature of their exchange reactions with rates in the order PPh$_2$Me < P(OPh)$_3$ < PPh$_3$; (bda)Fe(CO)$_2$PPhMe$_2$ shows no decomposition at 90°C over a period of days and in the presence of chd, shows no detectable exchange to give (chd)Fe(CO)$_2$PPhMe$_2$.

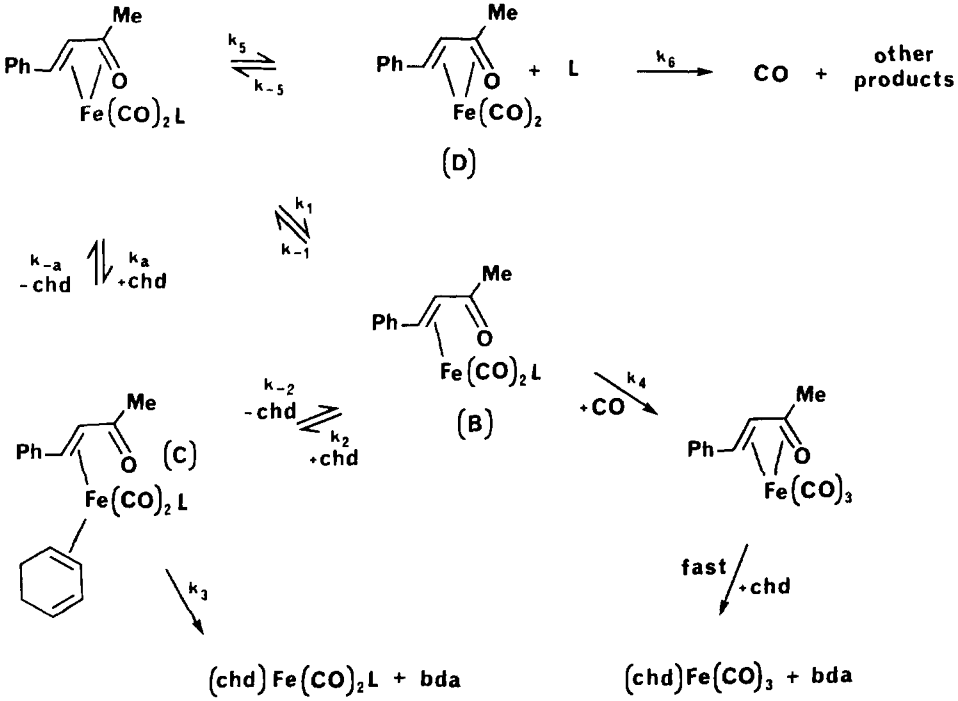
(ii) (bda)Fe(CO)$_2$PPh$_3$ reacts with chd under one atmosphere of CO at 70°C to give exclusively (chd)Fe(CO)$_3$. Although no (bda)Fe(CO)$_3$ can be detected by infrared sampling, the rapid reaction of (bda)Fe(CO)$_3$ with chd to give (chd)Fe(CO)$_3$ at this temperature may be noted.

(iii) Variations in entering and leaving groups have been investigated. Although (bda)Fe(CO)$_2$PPh$_3$ reacts with both 1,3,5-cycloheptatriene (chpt) and 1,3,5,7-

cyclooctatetraene (cot) to give (η^4-diene)Fe$(CO)_2PPh_3$ complexes, the reactions are sufficiently slow (compared to that using chd) that greatly increased substrate decomposition makes kinetic monitoring unhelpful. Although (cinn)Fe$(CO)_2PPh_3$ reacts more slowly with chd than its bda analogue to give (chd)Fe$(CO)_2PPh_3$, the larger amounts of (chd)Fe$(CO)_3$ also formed preclude any kinetic investigation. Qualitatively, the ordering of rates for the exchange bda > cinn is the same as that observed in the kinetically well behaved reactions of the (η^4-enone)Fe$(CO)_3$ complexes [2].

(b) Mechanism

A mechanism which best explains these qualitative and quantitative data is shown in Scheme 1.



SCHEME 1

The small amounts of (chd)Fe$(CO)_3$ that are formed in the absence of added CO are proposed to arise by a decomposition which proceeds via phosphine dissociation to yield intermediate D; decomposition of D, followed by the reaction of the released CO with (bda)Fe$(CO)_2$L, gives (bda)Fe$(CO)_3$ which under the conditions of temperature and concentration of chd used, rapidly yields (chd)Fe$(CO)_3$. Phosphine, rather than enone dissociation via intermediate B, is preferred as the thermolytic pathway for the following reasons:

(i) The ratio of (chd)Fe$(CO)_3$ decomposition products (91/9) in the exchange reaction is about the same as the ratio of the half-life of the exchange reaction to the half-life of the decomposition in the absence of chd (92/8). If both decomposition and exchange proceeded through intermediate B, one might expect some suppression of the decomposition in the presence of chd.

(ii) The ordering of the rates of decomposition $PPh_3 > PPh_2Me > PPhMe_2$ parallels that found for phosphine dissociation in the octahedral *cis*-$Mo(CO)_4(PPh_xMe_{3-x})_2$ series ($x = 1$–3) [9a,9b].

Formation of $(bda)Fe(CO)_3$ and inter alia, $(chd)Fe(CO)_3$ via reaction of CO with intermediate B rather than D is preferred for the following reasons:

(i) Reaction of $(bda)Fe(CO)_2PPh_3$ with chd under one atmosphere of CO results in exclusive formation of $(chd)Fe(CO)_3$. This most probably results from an effective competition of CO with chd for intermediate B. Although the situation is complicated by the complex nature of the rate law, data from other reactions do suggest at least some discrimination; k_2/k_{-1} values have been determined for the reaction

$$(PhCH{=}CH_2)Fe(CO)_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(CO)_4 + PhCH{=}CH_2 \xrightarrow[+L]{k_2} Fe(CO)_4L$$

where $L = CO$ and methyl acrylate [4a,10]. Assuming a constant value of k_{-1}, the value of $k_2(CO)/k_2$ (methyl acrylate) is approximately two.

(ii) Reaction of the related Schiff base complex (η^4-PhCH=CHCH=NPh)$Fe(CO)_2AsPh_3$ with CO also yields exclusively (η^4-PhCH=CHCH=NPh)$Fe(CO)_3$ [11] and the kinetic results are completely consistent with a rate-determining formation of an *N*-bound (η^2-PhCH=CHCH = NPh)$Fe(CO)_2AsPh_3$ intermediate analogous to B of Scheme 1. The data also indicate that coordination of CO to this *N*-bound intermediate is much favoured relative to rechelation, as k_{-1}/k_4 0.054 mol dm^{-3} for this complex.

Since the amount of decomposition is small in the absence of added CO, we have treated the kinetic data solely on the basis of the exchange pathway of Scheme 1 (i.e., k_5, k_{-5}, k_6 and $k_4 = 0$). The exchange pathway may be seen to involve competing reversible dissociative and I_d formation of intermediate C which is irreversibly transformed into $(chd)Fe(CO)_2L$. This mechanism is exactly that proposed for the diene exchange of $(bda)Fe(CO)_3$ [4a]. Steady state treatment of intermediates B and C yields the rate law

$$\frac{-d[S]}{dt} = [S]\left[k_\alpha[\text{chd}] + \frac{k_\beta[\text{chd}]}{k_\gamma + k_\delta[\text{chd}]}\right] \quad \text{where } S = (bda)Fe(CO)_2L$$

and thus

$$k_{\text{obs}} = k_\alpha[\text{chd}] + \frac{k_\beta[\text{chd}]}{k_\gamma + k_\delta[\text{chd}]}$$

where

$$k_\alpha = k_3k_a/(k_{-a} + k_3)$$

$$k_\beta = \frac{k_3(k_1k_2k_{-a} + k_1k_2k_3 - k_ak_{-2}k_{-1})}{k_{-a} + k_3}$$

$$k_\gamma = k_{-a}k_{-1} + k_{-2}k_{-1} + k_3k_{-1}$$

and

$k_{\delta} = k_{-a}k_2 + k_3k_2$

Plots of k_{obs} against [chd] for reactions of (bda)Fe(CO)$_3$ and (bda)Fe(CO)$_2$PPh$_3$ are shown in Fig. 1, while Fig. 2 shows more clearly the curvature in the plots of k_{obs} against [chd] for the phosphine and phosphite complexes. Although the simplifying assumptions that $k_{-a} = k_{-2} = 0$ have been used in the application of this mechanism to the substitution of (η^4-enone)Fe(CO)$_3$ complexes by Group V donors [12a–12d], the shapes of the curves of Figs. 1 and 2 indicate that no such simplification is warranted here. The derived rate constants (k_{α}, k_{β}/k_{δ} and k_{γ}/k_{δ}) listed in Table 2 were obtained by a fitting of the experimental data to the expression for k_{obs} above by means of a non-linear least squares program. Initial estimates were obtained graphically and then refined by an iterative Taylor differential correction routine. In addition, an overall standard deviation is given which reflects the fit of the experimental data to the theoretical model. The value of this standard deviation for each system is close to the standard deviation of the difference between duplicate runs, thus showing that within the acceptable precision of our experiments, the mechanistic model is consistent with our experimental results.

The complexity of the expressions associated with the derived rate constants makes a detailed analysis rather difficult. However, three major points may be made, based mainly on a comparison of k_{obs} values:

(i) A comparison of the curves for the reaction of (bda)Fe(CO)$_3$ with chd in toluene and 100–120 petroleum ether shows some dependence on solvent. Although overall k_{obs} values differ only slightly, there are marked changes in the partial rate constants (Table 2); k_{γ}/k_{δ} diminishes appreciably in toluene, while k_{α} shows a marked increase.

(ii) Enone lability in the phosphine and phosphite complexes is much lower than

TABLE 2

DERIVED RATE CONSTANTS FOR REACTIONS OF (bda)Fe(CO)$_2$L WITH 1,3-CYCLOHEXADIENE [a,b,c]

L	Solvent	Temp. (°C)	10^4k_{α} (dm^3 mol^{-1} s^{-1})	$10^4k_{\beta}/k_{\delta}$ (s^{-1})	$10^4k_{\alpha}/k_{\delta}$ (mol dm^{-3})	$10^4\sigma_{fit}$ (s^{-1})	$10^4\sigma_{re}$ (s^{-1})
CO	toluene	70.2	0.4(1.2)	28.6(1.1)	0.82(0.07)	0.45	0.29
CO	100–120 petroleum ether	70.4	18.5(4.6)	22.8(2.2)	0.04(0.01)	0.81	0.30
PPh$_3$	100–120 petroleum ether	70.1	0.42(0.11)	0.38(0.04)	0.1(0.2)	0.02	0.01
P(OPh)$_3$	100–120 petroleum ether	70.1	0.10(0.11)	0.47(0.04)	0.02(0.01)	0.02	0.01
PPh$_2$Me	120–160 petroleum ether	91.2	0.43(0.06)	0.25(0.02)	0.02	0.01	0.01

[a] Standard deviations in parentheses. [b] Overall standard deviation

$$\sigma_{fit} = \left\{ \sum_{i=1}^{n} \frac{[k_{obs}(calc) - k_{obs}(expt)]_i^2}{n-3} \right\}^{1/2}$$, where n is the number of experimental observations.

[c] Standard deviation of experimental reproducibility $\sigma_{re} = \sigma[k_{obs}(A) - k_{obs}(B)]$ where (A) and (B) are the duplicate determinations.

that of (bda)Fe$(CO)_3$. Crystal structure determinations of (cinn)Fe$(CO)_3$ [13], (cinn)Fe$(CO)_2PPh_3$ [14], and (bda)Fe$(CO)_2$L (L = $PPhMe_2$, PEt_3) [15] show that the complexes have a distorted square pyramidal structure with, in the cases of the phosphine derivatives, L occupying the axial site of the square pyramid. NMR results (see preceding paper [8]) show that at least for the bda complexes, this structure is essentially retained in solution. Although caution must be used in relating ground state structural and spectroscopic properties to reaction rates, a comparison of the crystal structures of (cinn)Fe$(CO)_3$ and (cinn)Fe$(CO)_2PPh_3$ is instructive. The latter shows shortened M–CO distances consistent with increased back donation which is also obvious from the infrared spectra, and although the M–enone bond distances are the same in both complexes, increased back donation to the enone is seen in changes in the enone bond distances, particularly an increased C=O bond length. Since exchange proceeds by competing D and I_d pathways in which breaking of the ketonic M–CO bond is important, this probably provides an electronic contribution to the decreased lability of the phosphine and phosphite complexes.

(iii) The ordering of exchange lability is in the order $PPh_3 \approx P(OPh)_3 > PPh_2Me \gg PPhMe_2$. For the phosphine complexes, the order follows the decreasing cone angle of the ligands (PPh_3 (145°) > PPh_2Me (136°) > $PPhMe_2$ (122°)). Although much slower, the rates of decomposition (which probably occurs via initial phosphine dissociation) exhibit the same ordering. Spectroscopic properties [8] (infrared and ^{13}C chemical shifts of the bound carbons) show no discernable trend in ground state electronic structure, and perhaps the most relevant data for comparison concern the reaction

$$cis\text{-}Mo(CO)_4L_2 + CO \rightarrow Mo(CO)_5L + L$$

which proceeds via phosphine dissociation at rates which are in the order $PPh_3 > PPh_2Me > PPhMe_2$ [9a,9b]. Crystal structures of these complexes [16] show increasing distortion from octahedral geometry with increasing cone angle of L, and thus the ordering of lability which we also observe seems best interpreted in terms of a steric acceleration involving an increasing relief of steric strain in proceeding either via the D process from S to B or via the I_d pathway from S to C (S = (bda)Fe$(CO)_2$L), which by definition involves substantial progress towards ketonic M–CO cleavage in the transition state.

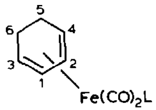
On the basis of only its cone angle (128°), a lower exchange lability might be predicted for (bda)Fe$(CO)_2P(OPh)_3$ than that which is actually found. However, infrared spectra indicate a significantly smaller back donation to CO than in (bda)Fe$(CO)_2PPh_xMe_{3-x}$ ($x = 1$–3), and if this is mirrored in a smaller back donation to the enone ligand as well, this may provide a lower electronic barrier to exchange for the $P(OPh)_3$ complex.

From a synthetic point of view, a paradox is apparent, at least for phosphine complexes, in that although ligands of large cone angle promote the fastest rates of enone exchange, they are also most liable to dissociation via loss of phosphine. One may, however, use this reaction to a possible advantage in enantioselective synthesis. Thus (Scheme 2), irradiation of $Fe(CO)_4L$ (L = (+)-Ph_2P(menthyl), (+)-$Ph_2PCH_2CH(Me)Et$) with benzylideneacetone yields the expected (bda)Fe$(CO)_2$L complexes. Only the (+)-$Ph_2PCH_2CH(Me)Et$ derivative has been obtained analytically pure; two equally intense signals are observed in the ^{31}P NMR spectrum,

(Continued on p. 94)

TABLE 3

MICROANALYTICAL AND SPECTROSCOPIC DATA

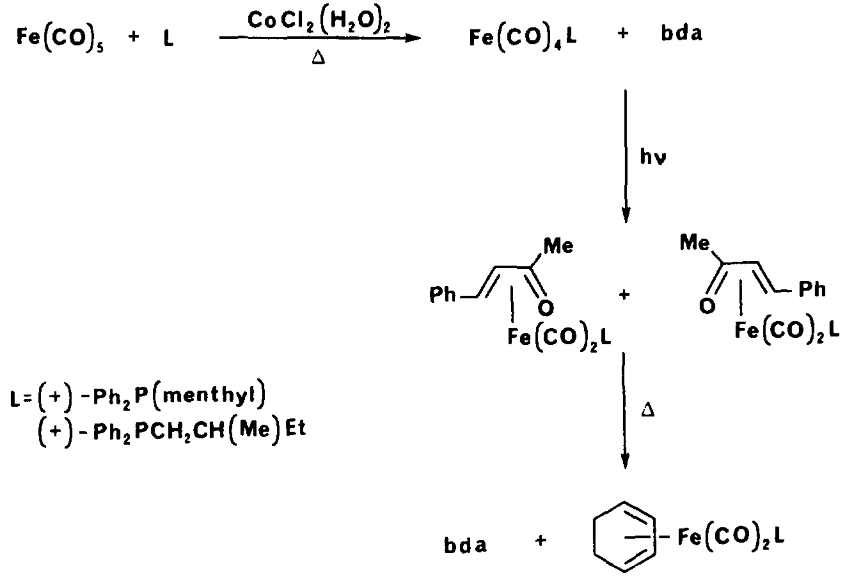
	Microanalysis (Found (calcd.) (%))		IR	^{13}C NMR [b]			^{31}P NMR [c]
	C	H	ν(CO) [a]		δ		δ
L = PPh_3	69.1	5.06	1975	1,2	84.6		70.2
	(68.8)	(4.81)	1922	3,4	61.1 (3.0)		
				5,6	24.7		
				Ph	128–133		
				CO	218.7 (13.6)		
L = $P(OPh)_3$	62.0	4.53	1998	1,2	83.3		173.2
	(62.2)	(4.62)	1942	3,4	61.1 (5.8)		
				5,6	23.7		
				Ph	121–129, 150.8		
				CO	215.0 (17.6)		
L = PPh_2Me	64.5	5.40	1975	1,2	84.2		
	(64.3)	(5.41)	1920	3,4	60.3 (2.9)		
				5,6	24.9		
				Ph	128–132		
				Me	20.0 (28.3)		
L = (+)-Ph_2P(menthyl)	69.9	7.45	1978	1,2	85.6		72.3
	(69.7)	(7.25)	1925		86.5		
				3,4	60.5 (2.9)		
					61.0 (2.0)		
				5,6	24.4		
					24.9		
				menthyl	17.1	28.8	
					20.4	30.3 (3.9)	
					21.3 (11.7)	31.0 (6.8)	
					24.0	38.9 (20.5)	
					28.0 (5.8)	39.7 (3.9)	
				Ph	127–135		

L = (+)-$Ph_2PCH_2CH(Me)Et$	67.2	6.70	1982	1,2	84.8		
	(67.0)	(6.53)	1927		84.7		62.9
				3,4	61.1		
					60.5 (3.9)		
				5,6	24.9		
					24.6 (2.0)		
				P–CH_2	39.2 (23.5)		
				CH	31.9		
				Et	31.5, 11.2		
				Me	21.2 (4.9)		
				Ph	127–132		
$Fe(CO)_4L$							
L = (+)-Ph_2P(menthyl)	63.4	5.85	2042	menthyl	17.5	28.4	68.9
	(63.4)	(5.95)	1977		20.8	30.2 (3.9)	
			1947		21.4 (12.6)	31.0 (6.8)	
			1937		23.9	39.1	
					28.3 (7.7)	41.4 (22.4)	
				Ph	128–135		
				CO	212.6 (15.7)		
L = (+)-$Ph_2PCH_2CH(Me)Et$	59.3	4.90	2051	P–CH_2	39.0 (28.4)		66.4
	(59.5)	(5.00)	1987	CH	31.7		
			1954	Et	31.4, 11.1		
			1947	Me	21.1 (5.8)		
				Ph	128–135		
				CO	212.6 (17.6)		
(bda)$Fe(CO)_2L$							
L = (+)-$Ph_2PCH_2CH(Me)Et$	67.9	6.06	1997				49.1
	(67.7)	(6.09)	1949				49.0
			1941				
L = (+)-Ph_2P(menthyl)			1997				
			1947				
			1939				

---

[a] Heptane solution (cm^{-1}). [b] $CDCl_3$ solution, ppm from TMS. [c] $CDCl_3$ solution, ppm from 85% H_3PO_4.

consistent with the presence of two diastereoisomers (Scheme 2). Three CO stretching vibrations are observed, rather than the two which are characteristic of (bda)Fe$(CO)_2$L complexes in which L is achiral. Infrared spectra of the (+)-Ph_2P(menthyl) complex are essentially identical. Both complexes easily undergo exchange with chd to give the (chd)Fe$(CO)_2$L complex, and we have recently shown that nucleophilic attack on the [(η^5-cyclohexadienyl)Fe$(CO)_2$L]BF_4 salt (L = (+)-Ph_2P(menthyl); prepared by hydride abstraction from (chd)Fe$(CO)_2$L) does proceed with a reasonable degree of asymmetric induction at the chiral quaternary carbon so formed [17].



SCHEME 2

Experimental

NMR and infrared spectra were recorded on JEOL FX-100 and Perkin–Elmer 257 spectrometers. Samples of (bda)Fe$(CO)_3$, (bda)Fe$(CO)_2$L (L = PPh_3, PPh_2Me, $PPhMe_2$, $P(OPh)_3$) and (cinn)Fe$(CO)_2PPh_3$) were prepared as described [8,15]. The purity of the substrates used in the kinetic work was confirmed by microanalysis. Spectroscopic and microanalytical data for other complexes may be found in Table 3. Solvents used in the kinetic work were distilled and degassed; chd, chpt and cot were used as received.

(a) Kinetic work

All kinetic experiments were conducted in duplicate under argon in sealed, darkened vessels immersed in a constant temperature oil bath (±0.01°C) at the temperatures given in Table 1. A sample of substrate was weighed into the reaction vessel, and after flushing and addition of solvent, the vessel was shaken in the constant temperature bath until solution was complete (the limits of solubility of the (bda)Fe$(CO)_2$L complexes are approached in these solvents). Appropriate volumes of diene were then added by syringe, and samples for infrared monitoring were periodically withdrawn by syringe, yielding an average of at least 12 absorbance, time data pairs.

Infrared spectra were recorded using 2 mm NaCl cells with a solvent/diene blank of appropriate concentration. k_{obs} values were obtained from plots of $\ln(A_0 - A_\infty)/(A_t - A_\infty)$ where A represents the absorbance of the highest frequency absorption of the (bda)Fe(CO)$_2$L or (bda)Fe(CO)$_3$ substrate. Due to the slowness of the reactions of the (bda)Fe(CO)$_2$L complexes, they were generally followed only to two half-lives; however, selected reactions followed to three half-lives showed no deviation from linearity for the plots of $\ln(A_0 - A_\infty)/(A_t - A_\infty)$ against time. All such plots had correlation coefficients greater than 0.999.

(b) Synthesis

(i) Fe(CO)$_4$[(+)-Ph$_2$PCH$_2$(Me)Et]

$CoCl_2(H_2O)_2$ (0.04 g, 0.24 mmol) and (+)-Ph$_2$PCH$_2$CH(Me)Et (1.95 g, 7.55 mmol) were added to toluene (30 ml) and the stirred solution brought to reflux. Fe(CO)$_5$ (2.96 g, 15.1 mmol) was added and the reaction mixture was refluxed until the infrared spectrum indicated completion of reaction (ca. 4.5 h). The catalyst and excess of phosphine were removed by eluting the cold reaction mixture through a $CoCl_2(H_2O)_6$/alumina/silica gel (5 g/20 g/20 g) column with benzene. Solvent and excess of Fe(CO)$_5$ were removed under reduced pressure and the residue was chromatographed on a silica gel column using light petroleum (40–60)/dichloromethane (90/10) as eluant to give a yellow oil (73%) which solidified on cooling. An analytical sample was obtained by sublimation (105–115°C, 0.02 mmHg).

Fe(CO)$_4$[(+)-Ph$_2$P(menthyl)] was prepared similarly.

(ii) (bda)Fe(CO)$_2$[(+)-PPh$_2$CH$_2$CH(Me)Et]

Fe(CO)$_4$[(+)-PPh$_2$CH$_2$CH(Me)Et] (0.658 g, 1.55 mmol) and benzylideneacetone (0.226 g, 1.55 mmol) were dissolved in benzene (200 ml) and irradiated for 22 h using a 90 W medium pressure lamp. After removal of solvent, the orange-red solution was chromatographed on silica gel using benzene. After elution of starting material, the product was eluted with benzene/ethyl acetate (90/10) and isolated as a red oil after removal of solvent (56% yield).

(bda)Fe(CO)$_2$[(+)-Ph$_2$P(menthyl)] was prepared similarly (65% yield), although satisfactory microanalyses could not be obtained.

(iii) (chd)Fe(CO)$_2$L complexes

The (bda)Fe(CO)$_2$L complex (300 mg) was reacted with a 40-fold molar excess of chd at 70°C in 100–120 petroleum ether (L = PPh$_3$, PPh$_2$Me, P(OPh)$_3$) or in refluxing toluene (L = (+)-Ph$_2$P(menthyl) or (+)-Ph$_2$PCH$_2$CH(Me)Et) until reaction was complete, as judged by the infrared spectrum. After filtration through Hiflow and evaporation of solvent, chromatography on silica gel using benzene gave the crude product which was crystallized from methanol (L = PPh$_3$, P(OPh)$_3$) to give light yellow crystals or sublimed (90°C/0.01 mmHg, L = PPh$_2$Me; 120°C/0.01 mmHg, L = (+)-Ph$_2$P(menthyl) or (+)-Ph$_2$PCH$_2$CH(Me)Et) to give yellow oils.

The identity of (chd)Fe(CO)$_3$ was confirmed by comparison of its infrared spectrum with that of an authentic sample (ν(CO): 2046, 1976 cm^{-1}, hexane).

Acknowledgement

We thank the SERC (M.J.T. and P.M.B.) and the Association of Commonwealth Universities (J.K.) for their support in the form of studentships.

References

1 (a) A.J. Pearson, Accts. Chem. Res., 13 (1980) 463; (b) A.J. Pearson, Trans. Met. Chem., 6 (1981) 67; (c) A.J. Pearson in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 8, ch. 58, Pergamon Press, 1982.

2 J.A.S. Howell, B.F.G. Johnson, P.L. Josty and J. Lewis, J. Organomet. Chem., 39 (1972) 329.

3 (a) G. Scholes, C.R. Graham and M. Brookhart, J. Amer. Chem. Soc., 96 (1974) 5665; (b) M. Brookhart, G.O. Nelson, G. Scholes and R.A. Watson, J. Chem. Soc., Chem. Commun., (1976) 195; (c) C.R. Graham, G. Scholes and M. Brookhart, J. Amer. Chem. Soc., 99 (1977) 1180; (d) M. Brookhart and G.O. Nelson, J. Organomet. Chem., 164 (1979) 193.

4 (a) P.M. Burkinshaw, D.T. Dixon and J.A.S. Howell, J. Chem. Soc., Dalton Trans., (1980) 999; (b) J.A.S. Howell and P.M. Burkinshaw, J. Organomet. Chem., 152 (1978) C5.

5 B.F.G. Johnson, J. Lewis, G.R. Stephenson and E.J.S. Vichi, J. Chem. Soc., Dalton Trans., (1979) 369.

6 B.M.R. Bandara, K. Chamberlain, P. Dahler, A.I. Day, I.D. Jenkins, L.F. Keely, T.C. Khor, G. Kretschmer, A.J. Liepa, A.S. Narula, W.D. Raverty, E. Rizzardo, C. Sell, G.R. Stephenson, D.J. Thompson and D.H. Williamson, Tetrahedron, 37 (1981) 289, (supplement 1).

7 (a) J.A.S. Howell, B.F.G. Johnson, R. Edwards and J. Lewis, J. Chem. Soc., Dalton Trans., (1974) 2105; (b) A.J. Pearson, S.L. Cole and B. Chen, J. Amer. Chem. Soc., 105 (1983) 4483.

8 D.T. Dixon, J.A.S. Howell and J. Kola, J. Organomet. Chem., 266 (1984) 69.

9 (a) D.J. Darensbourg and A.H. Graves, Inorg. Chem., 18 (1979) 1257; (b) D.J. Darensbourg, R. Kudaroski and W. Schenk, Inorg. Chem., 21 (1982) 2488.

10 G. Cardaci, Inorg. Chem., 13 (1974) 368.

11 G. Bellachioma, G. Reichenbach and G. Cardaci, J. Chem. Soc., Dalton Trans., (1980) 635.

12 (a) G. Cardaci and S. Sorriso, Inorg. Chem., 15 (1976) 1242; (b) G. Cardaci and G. Concetti, J. Organomet. Chem., 90 (1974) 49; (c) G. Cardaci and G. Bellachioma, J. Chem. Soc., Dalton Trans., (1977) 2181; (d) G. Cardaci and G. Bellachioma, Inorg. Chem., 16 (1977) 3099.

13 A. de Cian and R. Weiss, Acta Cryst., 28B (1972) 3273.

14 M. Sacerdoti, V. Bertolasi and G. Gilli, Acta Cryst., 36B (1980) 1061.

15 M. McPartlin, E.J.S. Vichi and P.R. Raithby, J. Organomet. Chem., 256 (1983) 111.

16 F.A. Cotton, D.J. Darensbourg, S. Klein and B.W.S. Kolthammer, Inorg. Chem., 21 (1982) 294.

17 J.A.S. Howell and M.J. Thomas, J. Chem. Soc., Dalton Trans., (1983) 1401.