Mechanism of the Reaction of Chelated Tricarbonyliron Complexes of α,β-Unsaturated Schiff Bases with Group 5 Ligands

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The complexes [$Fe(CO)_3(\eta$-$PhCH=CH-CH=N-C_6H_4X)$] (X = H, or 4-NMe$_2$, -OMe, -Me, or -Br) react with phosphine ligands to give [$Fe(CO)_2L$ (η-$PhCH=CH-CH=N-C_6H_4X)$]. The preparation of the phosphine derivatives is described. The kinetics of substitution by the phosphine ligands L (PPh$_3$ or PBu$^n{}_3$) are first order in the complex concentration and the pseudo-first-order rate constants vary with ligand concentration. The dependence of the rate constant on the concentration of ligand and the effects of temperature, of substituent X, and of the nature of ligand L point to a reaction mechanism having two paths, one associative with the ligand and the other dissociative involving a rapid $\eta^4 \rightleftharpoons \sigma$ equilibrium of the reagent complex.

COMPLEXES of tricarbonyliron with 1,3-diene ligands are inert in organic solvents of low polarity and only under drastic conditions (*e.g.* high temperature [1]) is the formation of substituted complexes with Group 5 ligands observed. In order to obtain information on the reactivity of these complexes, we have undertaken a study of the mechanisms of their reaction with Group 5 ligands. Since the iron–heterodiene bond is much more labile than the iron–diene bond, we studied the complexes of tricarbonyliron with α,β-unsaturated aldehydes.[2,3] The results obtained indicate that the reaction mechanism involves a dissociative stage of the η^4-heterodiene complexes to unsaturated η^2 complexes.

TABLE 1

Analytical data and CO stretching frequencies of the complexes [$Fe(CO)_2L(\eta$-$PhCH=CH-CH=N-C_6H_4X)$]

			Analysis (%)						
			Calc.			Found			
L	X	M.p. (θ_c/°C)	C	H	N	C	H	N	$\bar{\nu}$(CO) (in n-hexane) / cm^{-1}
PPh$_3$	H	163—165	73.6	3.20	2.45	73.1	3.30	2.65	1 942, 1 997
	4-Me	148—150	73.85	3.45	2.40	73.6	3.50	2.10	1 941, 1 997
	4-Cl	158—160	69.4	2.85	2.30	69.5	2.60	2.30	1 941, 1 996
	4-Br	156—159	64.65	2.65	2.15	64.2	2.55	2.35	1 942, 1 998
	4-I	160—163	60.3	2.45	2.00	59.85	2.20	2.05	1 945, 1 998
	4-OMe	148—151	71.9	3.35	2.35	71.5	3.60	2.25	1 941, 1 997
	4-NMe$_2$	141—143	72.35	3.75	4.55	72.05	3.90	4.80	1 944, 1 994
AsPh$_3$	H	136—137	68.3	2.95	2.30	68.6	2.75	2.20	1 941, 1 997
SbPh$_3$	H	150—151	63.5	2.75	2.10	63.2	2.85	2.00	1 939, 1 996

We now describe the results of a study of [$Fe(CO)_3$-(η-$PhCH=CH-CH=N-C_6H_4X)$] (X = H or 4-NMe$_2$, -OMe, -Me, or -Br) with the aim of confirming the behaviour observed for the α,β-unsaturated aldehydes in the case of the present α,β-unsaturated Schiff-base ligands.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer using 0.5-mm NaCl cells. The Schiff bases were prepared by adding dropwise a solution of aniline, or one of its derivatives, in diethyl ether to a diethyl ether solution of cinnamaldehyde. The solution was concentrated and the Schiff base crystallised. The complexes [$Fe(CO)_3(\eta$-$PhCH=CH-CH=N-C_6H_4X)$] were prepared as described in ref. 4. Reactions involving carbon monoxide [5] were carried out at atmospheric pressure using a thermostatted burette to maintain constant pressure.[6]

Preparation of the Complexes.—[$Fe(CO)_2(PPh_3)(\eta$-$PhCH=CH-CH=N-C_6H_4X)$] (1). Complex (1; X = H) was prepared as in the literature.[7] Complexes (1; X = 4-Me, -OMe, -Br, -I, -Cl, or -NMe$_2$) were prepared as follows.

The complex [$Fe(CO)_3(\eta$-$PhCH=CH-CH=N-C_6H_4X)$] (0.5 g) and PPh$_3$ (0.5 g) (mol ratio 1 : 1.5) were dissolved in deaerated toluene (50 cm^3) and allowed to react at 70 °C. Reaction was complete after 1.5 h. Complexes (1; X = 4-Cl, -Br, or -I), were obtained almost pure with only trace amounts of [$Fe(CO)_3(PPh_3)_2$] and were further purified by recrystallisation from dichloromethane–n-hexane (yield 70%). For X = 4-Me, -OMe, or -NMe$_2$, appreciable quantities of [$Fe(CO)_3(PPh_3)_2$] were obtained. In these cases, purification was performed chromatographically on a neutral Al$_2$O$_3$ column using CH_2Cl_2–C_6H_{14} as eluant. The pure complexes (1) were then obtained by further crystallisation of the desired fraction from CH_2Cl_2–C_6H_{14} (yield 50%). Elemental analysis, i.r. spectra in n-hexane, and some physical properties of complexes (1) are listed in Table 1.

[$Fe(CO)_2(AsPh_3)(\eta$-$PhCH=CH-CH=NPh)$] (2). The complex [$Fe(CO)_3(\eta$-$PhCH=CH-CH=NPh)$] (0.5 g) and AsPh$_3$ (6.0 g) (mol ratio 1 : 10) were allowed to react at 60 °C in deaerated toluene for 24 h. The reaction was still not

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complete after this time, but the rate of reaction became very slow and the reaction was interrupted. As well as complex (2), comparable quantities of $[Fe(CO)_3(AsPh_3)_2]$ were also obtained. The solid was chromatographed on neutral Al_2O_3 using CH_2Cl_2–C_6H_{14} as eluant in order to eliminate the reagent complex which is eluted first. The complex $[Fe(CO)_3(AsPh_3)_2]$ was separated from (2) as with complexes (1), yield 30%.

$[Fe(CO)_2(SbPh_3)(\eta\text{-Ph–CH=CH–CH=NPh})]$ (3). The complex $[Fe(CO)_3(\eta\text{-Ph–CH=CH–CH=NPh})]$ (0.5 g) and $SbPh_3$ (3.5 g) (mol ratio 1 : 5) were allowed to react at 60 °C for 15 h after which the reaction was 80% complete. The product consisted of 60% complex (3) and 20—30% of $[Fe(CO)_3(SbPh_3)_2]$. The two complexes were separated chromatographically as described above for (2).

TABLE 2

Kinetic data for reaction (1) in toluene with the complex $[Fe(CO)_3(\eta\text{-PhCH=CH–CH=NPh})]$

θ_c/°C	L	$10^2[L]$/mol dm^{-3}	10^4k_I/s^{-1}	10^3k_{II}/dm^3 mol^{-1} s^{-1}	$10^{-2}(k_{II} - k_a)^{-1}$/mol dm^{-3} s	$(1 - \alpha) : \alpha$
49.5	PPh_3	1.97	1.14	5.79	1.8	0.08
		4.18	1.24	2.97	3.4	0.13
		6.05	1.28	2.12	4.9	0.17
		8.03	1.31	1.63	6.4	0.21
		10.03	1.32	1.32	7.9	0.25
		24.43	1.42	0.58	19.1	0.59
		36.13	1.50	0.42	27.9	0.84
		66.39	1.66	0.25	51.7	
60.0		2.02	4.48	22.18	4.5	0.06
		2.18	4.53	20.82	4.8	0.08
		6.02	5.17	8.59	11.9	0.15
		10.46	5.19	4.96	20.8	0.34
		16.75	5.55	3.32	31.7	0.50
		19.98	5.53	2.76	38.5	0.63
		50.61	6.33	1.25	91.7	
		100.54	7.12	0.71	181.8	
70.2		1.82	14.2	77.9		
		3.93	16.6	42.3		
		6.12	18.3	29.9		
		8.35	18.5	22.2		
60.0	PBu^n_3	5.05	4.66	9.22	1.3	
		7.46	5.75	7.71	1.6	
		8.23	5.81	7.06	1.8	
		10.19	5.92	5.8	2.35	
		14.76	7.34	4.9	2.93	
		19.86	7.66	3.9	4.35	
		37.95	11.81	3.1	6.45	
		72.29	18.39	2.6	9.90	
		97.06	22.04	2.3	14.08	
		147.99	28.36	1.9	27.78	

Kinetic Measurements.—The kinetic runs were carried out in deaerated anhydrous toluene (by distillation over Na) in thermostatted vessels (±0.1 °C) fitted with a rubber cap, from which aliquot portions were withdrawn at chosen time intervals using a hypodermic syringe. The stoicheiometry of the reaction is as in (1) in which α is the

$$\begin{aligned}&[Fe(CO)_3(\eta\text{-PhCH=CH–CH=N–}C_6H_4X)] + (2-\alpha)PPh_3 \longrightarrow\\ &\quad \alpha[Fe(CO)_2(PPh_3)(\eta\text{-PhCH=CH–CH=N–}C_6H_4X)] +\\ &\qquad (1-\alpha)[Fe(CO)_3(PPh_3)_2] + \alpha CO +\\ &\qquad\quad (1-\alpha)PhCH{=}CH{-}CH{=}N{-}C_6H_4X \qquad (1)\end{aligned}$$

fraction of complex (1) obtained per mol of reagent complex. In some cases the ratio $(1 - \alpha) : \alpha$ was obtained from the ratio of the intensities of the corresponding i.r. bands of $[Fe(CO)_3(PPh_3)]$ and of (1). This ratio remained constant during the course of the reaction, but varied with the concentration of PPh_3. The concentrations of the complexes were determined using i.r. techniques, following the bands at *ca.* 2 060 cm^{-1} for $[Fe(CO)_3(\eta\text{-PhCH=CH–CH=N–}C_6H_4X)]$, the band at *ca.* 1 940 cm^{-1} for (1), and that at 1 880 cm^{-1} for $[Fe(CO)_3(PPh_3)_2]$.

The rate constants were always determined for reactions in the presence of a large excess of ligand (>10-fold) in order to give pseudo-first-order conditions. They were obtained by following both the disappearance of the reagent complexes [plotting $\ln(D_0/D_t)$ against t, where D_0 and D_t are the initial absorbance and that at time t of the reagent complex] and the appearance of complexes (1) and of $[Fe(CO)_3(PPh_3)_2]$ {plotting $\ln[D_\infty/(D_\infty - D_t)]$ against t, in which D_∞ and D_t are the absorbances of these complexes at the end of the reaction and at time t}. Values of the rate constants obtained from the appearance of complexes (1) and of $[Fe(CO)_3(PPh_3)_2]$ are the same within experimental error; values obtained from the disappearance of the reagent and those from the appearance of the products were the same within 5%. The kinetics were followed to at least four half-lives, at temperatures between 50 and 70 °C.

RESULTS AND DISCUSSION

Reaction (1) was followed kinetically for complexes with X = H, 4-Me, -OMe, $-NMe_2$, or -Br and with the ligands L = PPh_3 or PBu^n_3. The results are shown in Tables 2 (X = H, L = PPh_3 or PBu^n_3) and 3 (X = 4-NMe_2, -OMe, -Me, or -Br; L = PPh_3). Reactions with $AsPh_3$ and $SbPh_3$ could not be studied kinetically since they did not go to completion. In contrast to the case of α,β-unsaturated heterodiene aldehydes which form the intermediates $[Fe(CO)_3L(\eta^2\text{-heterodiene})]$,[8] the probable explanation for this fact lies in a reaction of the

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[8] A. Vessieres and P. Dixneuf, *Tetrahedron Letters*, 1974, 1499.

TABLE 3

Kinetic data for reaction (1) in toluene with L = PPh_3

X	θ_c/°C	$10^2[PPh_3]$/mol dm^{-3}	10^4k_I/s^{-1}	10^3k_{II}/dm^3 mol^{-1} s^{-1}	$10^{-1}(k_{II} - k_a)^{-1}$/mol dm^{-3} s	$(1 - \alpha) : \alpha$
4-NMe_2	49.5	5.33	4.00	7.50	13.7	0.22
		10.08	4.28	4.25	24.6	0.38
		15.15	4.68	3.09	34.3	0.50
		24.97	5.11	2.05	53.4	0.93
		35.12	5.46	1.55	72.8	1.30
		47.28	5.69	1.20	97.8	
		62.59	5.96	0.95	129.4	
		93.27	6.54	0.70	191.2	
	60.0	5.07	14.2	27.9	3.6	
		10.14	15.9	15.7	6.5	
		15.77	17.2	10.9	9.4	
		25.67	18.7	7.3	14.2	
		34.96	19.0	5.4	19.5	
		51.24	19.4	3.8	28.4	
		60.26	19.8	3.3	33.3	
4-OMe		5.07	7.92	15.62	6.6	0.16
		10.09	8.43	8.36	12.6	0.32
		15.00	8.76	5.84	18.4	0.42
		24.96	9.31	3.73	30.2	0.52
		34.10	9.71	2.85	41.0	0.96
		42.86	10.28	2.39	50.6	1.16
		55.88	11.02	1.97	64.3	
		66.17	11.20	1.67	79.6	
		74.91	11.65	1.55	87.9	
4-Me		5.31	6.05	11.3	8.7	0.16
		10.05	6.47	6.44	15.8	0.29
		14.88	6.90	4.64	22.2	0.41
		25.30	7.33	2.90	36.0	0.66
		35.13	7.34	2.08	51.2	0.94
		43.51	7.85	1.80	60.6	1.13
		52.83	7.86	1.48	73.0	
		64.24	8.05	1.22	91.6	
		75.62	8.43	1.11	104.2	
4-Br		5.09	3.77	7.38	13.9	
		10.12	4.07	4.02	26.3	
		16.52	4.11	2.49	44.0	
		25.28	4.60	1.82	62.4	
		35.29	4.85	1.38	86.3	
		62.29	5.43	0.87	152.7	

final complexes (2) and (3) with the carbon monoxide obtained from reaction (1), to give the starting complex. That this is indeed the case was confirmed by treating the final complex (1) with CO when the starting tricarbonyliron complex was obtained.

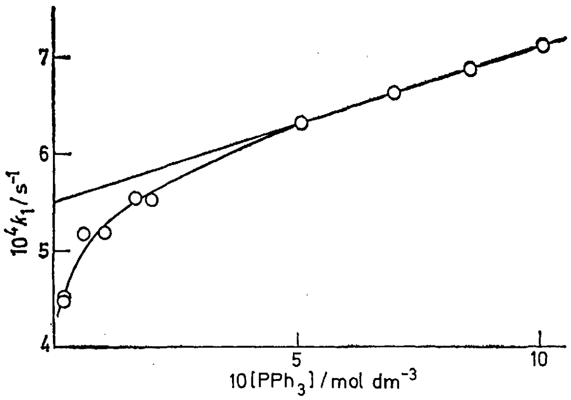


FIGURE 1 Plot of k_I against $[PPh_3]$ for reaction (1) (X = H) in toluene at 60 °C

All the reactions with L = PPh_3 and PBu^n_3 are pseudo-first order in ligand concentration. The pseudo-first-order rate constant (k_I, Tables 2 and 3) and $k_{II} = k_I/[L]$ vary with the concentration of the phosphine ligand. The behaviour of k_I with $[PPh_3]$ is shown in Figure 1 for $[Fe(CO)_3(\eta\text{-}PhCH{=}CH{-}CH{=}NPh)]$. The trend of k_{II}^{-1} is shown in Figure 2.

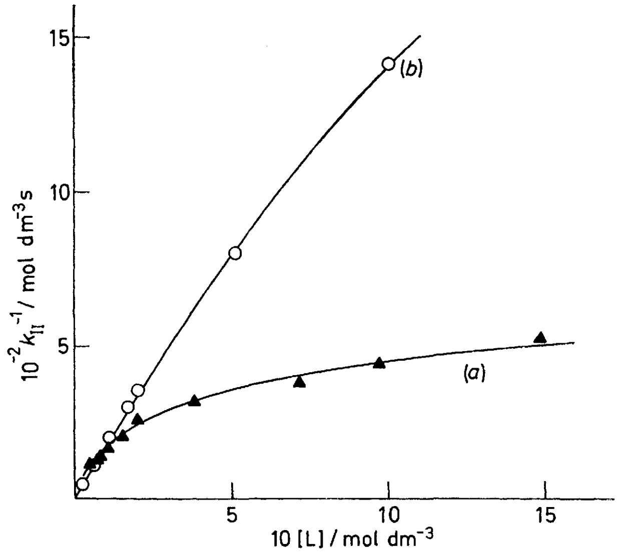
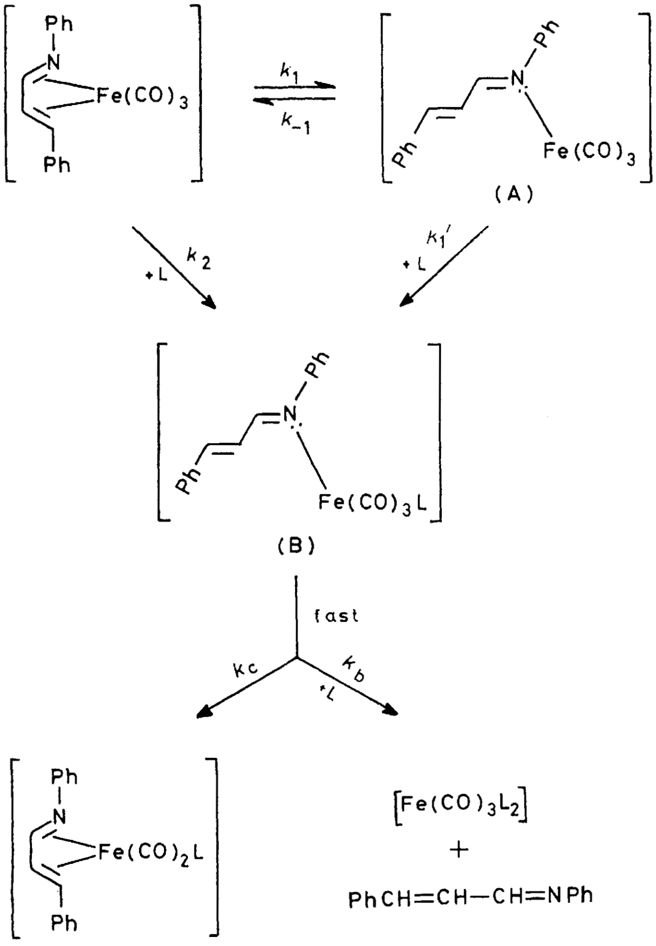


FIGURE 2 Plot of k_{II}^{-1} against [L] for reaction (1) (X = H) in toluene at 60 °C. L = PBu^n_3 (*a*) and PPh_3 (*b*)

As mentioned above, during reaction (1) we did not detect intermediate complexes [Fe(CO)$_3$L(η^2-PhCH=CH–CH=N–C$_6$H$_4$X)]; however, this does not exclude their formation. Such a possibility is supported by the fact that the complexes [Fe(CO)$_3$(η-PhCH=CH–CH=N–C$_6$H$_4$X)] react with carbon monoxide to form [Fe(CO)$_4${N(C$_6$H$_4$X)=CH–CH=CHPh}] which have a bond between the iron and the lone pair on the nitrogen atom.[9]

The results in Figures 1 and 2 suggest an extension of the mechanism found previously for the reaction of [Fe(CO)$_3$(η-C$_6$H$_4$X–CH=CH–CHO)] complexes with Group 5 ligands [3] to the present complexes, as shown in the Scheme. The structure of intermediates (A) and (B) (σ complexes) are arrived at on the basis of those for Schiff-base tetracarbonyliron complexes formed in the reaction of tricarbonyliron complexes with carbon monoxide.[9] A complete treatment of the mechanism, assuming that the steady-state approximation may be applied to the intermediates (A) and (B), gives the rate law (2) in which the constants refer to the Scheme



$$v = \frac{k_1 k_1'[\mathrm{L}][\mathrm{C}]}{k_{-1} + k_1'[\mathrm{L}]} + k_a[\mathrm{L}][\mathrm{C}] \qquad (2)$$

and [C] is the concentration of the reagent complex. The pseudo-first-order rate constant is given by expression (3) which accounts for the behaviour shown in Figure 1; thus, for very large [L], at which $k_1'[\mathrm{L}] \gg k_{-1}$, equation (3) reduces to $k_1 + k_a[\mathrm{L}]$. From the gradient of the linear part of the plot in Figure 1 it is possible to calculate k_a, while the intercept of this line gives k_1. These values are reported in Table 4 for the various complexes.

$$k_{\mathrm{I}} = \frac{k_1 k_1'[\mathrm{L}]}{k_{-1} + k_1'[\mathrm{L}]} + k_a[\mathrm{L}] \qquad (3)$$

Dividing both sides of equation (3) by [L] we obtain (4) which rationalises the behaviour shown in Figure 2, *i.e.* as [L] tends to infinity an asymptotic value of k_a is obtained [curve (*a*)]; with PPh$_3$ the asymptotic value is not obtained because of the lower basicity of this ligand [curve (*b*)].

$$\frac{k_{\mathrm{I}}}{[\mathrm{L}]} = k_{\mathrm{II}} = \frac{k_1 k_1'}{k_{-1} + k_1'[\mathrm{L}]} + k_a \qquad (4)$$

Further confirmation of the validity of the rate law was obtained by transferring k_a to the left-hand side of (4) and inverting to give equation (5). Figure 3 illustrates the behaviour of the left-hand side of equation (5) as a function of [PPh$_3$]. From the linear plot found it is possible to obtain values of k_{-1}/k_1' (Table 4).

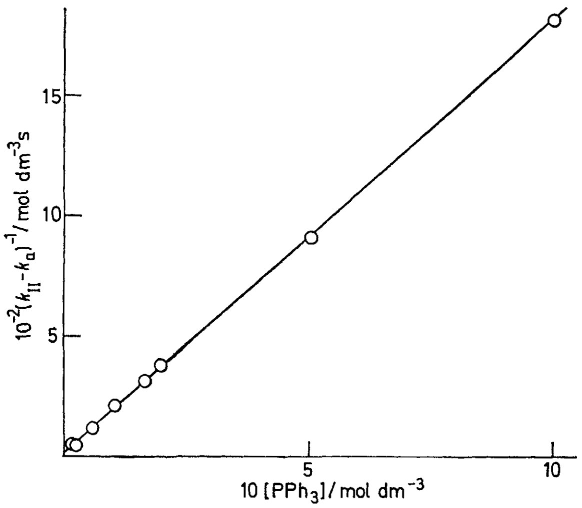


FIGURE 3 Plot of $(k_{\mathrm{II}} - k_a)^{-1}$ against [PPh$_3$] for reaction (1) (X = H) at 60 °C in toluene

$$\frac{1}{k_{\mathrm{II}} - k_a} = \frac{k_{-1}}{k_1 k_1'} + \frac{[\mathrm{L}]}{k_1} \qquad (5)$$

Further confirmation of the proposed mechanism comes from the effects of the nucleophilic ligands L and Schiff-base substituents X on the rate constants of Table 4. The nucleophilicity of the phosphine ligand affects the associative stage of the mechanism. Thus, the k_a value at 60 °C for X = H and L = PBu$^n_3$ (1.49 × 10^{-3} dm^3 mol^{-1} s^{-1}) is *ca.* 10 times greater than that for

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[9] G. Bellachioma and G. Cardaci, *J.C.S. Dalton*, 1977, 909.

L = PPh_3 (1.60×10^{-4} dm^3 mol^{-1} s^{-1}). Variations of this magnitude for these two ligands have been found in associative processes with other carbonyl complexes.[10] In contrast, the nature of the ligand has no influence on the dissociative process. The rate constants k_1 at 60 °C found for the complexes with X = H for L = PBu^n_3 (5.10×10^{-4} s^{-1}) and for PPh_3 (5.55×10^{-4} s^{-1}) are in agreement with this mechanism. The $-\log k_1$ values vary linearly with the Hammett σ_p values of the substituent X.[11] Electron-donor substituents accelerate the dissociation reaction, since they destabilise the reagent complexes, reducing the amount of π back bonding.[12]

TABLE 4

Summary of the kinetic results for reaction (1) in toluene

X	L	$\frac{\theta_c}{°C}$	$\frac{10^4 k_1}{s^{-1}}$	$\frac{10^4 k_a}{dm^3\ mol^{-1}\ s^{-1}}$	$\frac{10^2\ k_{-1}}{k_1'}$	$\frac{k_b}{k_c}$
4-NMe_2 [a]	PPh_3	60.0	18.7	2.75	1.87	
		49.5	4.90	1.77	2.07	3.69
4-OMe			8.42	4.13	0.51	2.75
4-Me			7.06	1.50	1.41	2.63
H [b]			1.27	0.58		2.22
		60.0	5.55	1.60	1.11	3.12
		70.2	20.3		0.75	
	PBu^n_3	60.0	5.10	14.9	1.27	
4-Br	PPh_3		4.13	2.17	0.83	

[a] The activation parameters of the dissociative step are $\Delta H_1^\ddagger = 25.5 \pm 1$ kcal mol^{-1} and $\Delta S_1^\ddagger = +5 \pm 3$ cal K^{-1} mol^{-1} (1 cal = 4.184 J). [b] The activation parameters of the dissociative step are $\Delta H_1^\ddagger = 31.3 \pm 1$ kcal mol^{-1} and $\Delta S_1^\ddagger = 20 \pm 3$ cal K^{-1} mol^{-1}. Those of the associative step are $\Delta H_a^\ddagger = 20 \pm 1$ kcal mol^{-1} and $\Delta S_a^\ddagger = -16 \pm 3$ cal K^{-1} mol^{-1}.

The rate constants of the associative process (k_a) are very inaccurate for the substituents 4-NMe_2 and -OMe, because of the small contribution of this process compared to that of the dissociative one. For the other substituents, the variations are small and the k_a values increase with increase in electron-attracting power of the substituents, as expected for an associative process. Apart from the substituent 4-OMe, values of k_{-1}/k_1' increase with the electron-donor power of the substituent and decrease with increase in temperature. The substituent effect may be explained by an increase in the electron density on the central metal of intermediate (A), which inhibits the nucleophilic reaction with the entering phosphine, thus decreasing k_1'. This effect, which also acts on the constant k_{-1}, may in this case be smaller because of the formation of a π bond, which is favoured by a larger electron density on the central metal.

The activation parameters (Table 4) for the complex $[Fe(CO)_3(\eta\text{-}PhCH{=}CH{-}CH{=}NPh)]$ are in agreement with the reaction Scheme. Thus, the dissociative process implies high values for enthalpies of activation ($\Delta H_1^\ddagger$) and positive entropies of activation ($\Delta S_1^\ddagger$); the associative process requires low activation energies ($\Delta H_a^\ddagger$) and negative entropies of activation ($\Delta S_a^\ddagger$), in good agreement with the experimental values.

In conclusion, the mechanism proposed is supported by the rate law, which takes account of all the experimental results, of the effects of the Schiff-base substituent X and of the entering nucleophilic ligands L on the rate constants, and, finally, of the activation parameters. The general behaviour is thus similar to that found for the corresponding complexes with α,β-unsaturated aldehydes. The dissociative reaction path accounts for the fact that these complexes decompose in solution, although they are stable for a long time in the solid state.

The $(1 - \alpha) : \alpha$ ratios reported in Tables 2 and 3 provide information on the mechanism by which intermediate (B) gives rise to both (1) and $[Fe(CO)_3L_2]$.[13] The values vary linearly with $[PPh_3]$, with a zero intercept, in the limits of experimental error. Assuming the mechanism in the Scheme, if the mode of formation of (1) from (B) is an intramolecular chelation and $[Fe(CO)_3L_2]$ is formed *via* an associative mechanism with the ligand, the ratio $(1 - \alpha) : \alpha$ should obey equation (6), which accounts for the linear behaviour. The

$$(1 - \alpha) : \alpha = (k_b/k_c)[PPh_3] \qquad (6)$$

gradients of plots of equation (6) allow k_b/k_c to be calculated (Table 4). This quantity is influenced only slightly by the substituent, the distance from the reaction centre being large and the effects involved partially compensating one another.

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