Kinetic Study of Ligand-substitution Reactions of (1—3-η-Allyl)dicarbonylnitrosyliron Complexes: Factors Affecting the Stability of σ- and η-Allyl Complexes

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The 1—3-η-allyl complexes [(η-C_3H_4X)Fe$(CO)_2$NO] (I; X = 1-Me, 1-Ph, and 2-Me) react with phosphine ligands [L = PPh_3 or $P(OEt)_3$] *via* a second-order associative mechanism to give [(η-C_3H_4X)Fe(CO)(NO)L], (II); for X = 2-Me and L = PPh_3, a parallel first-order dissociative route is operative. For X = 1-Cl, 1-CN, 2-Cl, and 2-Br intermediate five-co-ordinate complexes [(σ-C_3H_4X)Fe$(CO)_2$(NO)L], (III), are formed by a second-order associative process with the ligand [L = PPh_3, PBu^n_3, PPh_2Et, $P(OEt)_3$, or P{$(OCH_2)_3$OEt}]. Species (III) then rearrange to [(σ,η-(C_3H_4X)Fe(CO)(NO)L], (IV), *via* a first-order associative intramolecular chelation, with loss of CO. The above process with $P(OEt)_3$ shows a parallel second-order path of ligand disubstitution *via* CO insertion between the metal atom and the σ-allyl group, to give but-3-enoyl complexes, (V). Activation parameters for these processes have been estimated; the influence of the X substituents and of the entering L ligands has been examined.

FORMATION of σ-allyl iron complexes, by reacting 1—3-η-allyl derivatives [(η-C_3H_4X)Fe$(CO)_2$NO], (I), with phosphine ligands (L), has been recently described.[1,2] The results so far obtained suggest that: (*a*) for X = H, 1- and 2-Me, or 1-Ph a carbonyl ligand is substituted by phosphine to give [(η-C_3H_4X)Fe(CO)(NO)L], (II), with no analytical or kinetic [3] indication of the presence of the σ-allyl complexes (rearrangement of the σ-allyl intermediate to the η-allyl product may be very fast compared to its rate of formation); (*b*) for X = 1-CN, 1- and 2-Cl, or 2-Br, five-co-ordinate complexes [(σ-C_3H_4X)-Fe$(CO)_2$(NO)L], (III), are formed which chelate to [(σ,η-C_3H_4X)Fe(CO)(NO)L], (IV); (*c*) for X = 1- or 2-Cl and 2-Br and L = $P(OR)_3$ (R = Me or Et) a process similar to chelation occurs [see (*b*) above] in which simultaneous formation of disubstituted but-3-enoyl complexes, (V), occurs *via* CO insertion between the metal atom and the σ-allyl group.

The present kinetic work provides further information on the mechanism of the above reactions and the effect of varying the substituent X and ligand L. Factors which affect the stability of the σ-allyl complexes have also been studied; this subject has been the source of some recent controversy,[4,5] but the lack of an adequate number of such complexes, with a sufficiently wide range of electronic properties in the X and L groups, has so far prevented their detailed study.[6]

EXPERIMENTAL

The complexes were prepared and purified as previously reported.[2] Only one σ-allyl complex, (III), could be isolated and purified, due to the general instability of these complexes and their tendency [2] to react further with loss of CO and chelation. Therefore they were identified (in solution) by i.r. and n.m.r. methods. The phosphine ligands were commercial products used without further purification, except for liquids which were distilled as before.

Toluene, desiccated over sodium metal and deaerated, was used throughout as the solvent for the kinetic work. Temperatures employed ranged from 0 to 50 °C, depending on the rate of the specific reactions. Below 20 °C kinetics were followed in NaCl cells thermostatted by circulation of fluid, while at higher temperatures sealed ampoules were used from which aliquot portions were withdrawn at appropriate intervals of time by means of a syringe. An i.r. analytical method was generally adopted, using a Perkin-Elmer model 257 instrument and 0·5 mm NaCl cells. Whenever possible, the higher-frequency CO-stretching bands, both of the reacting and of the newly formed complex, were followed. When the σ-allyl intermediate, (III), was detected, the subsequent chelation step was monitored after complete formation of intermediate. In the few cases in which these two steps were well separated, the kinetics were studied also by u.v. spectroscopy using a Unicam SP 500 instrument with 1 cm quartz cells and following the decrease of absorbance at 510 nm. Figure 1 compares i.r. spectra in toluene solution of complexes (I; X = 2-Cl), (III; X = 2-Cl, L = PPh_3), and (IV; X = 2-Cl, L = PPh_3). Figure 2 shows the change in u.v. spectrum on formation of complex (III) from (I; X = 2-Cl) and $P(OEt)_3$.

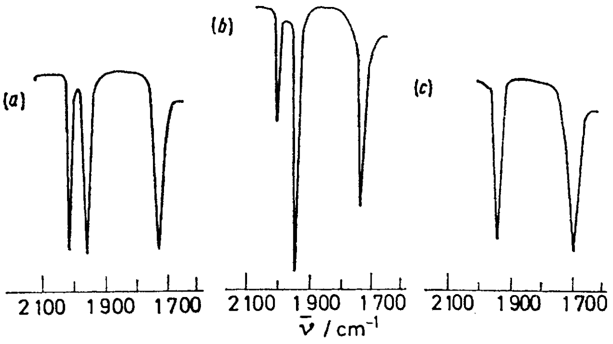

FIGURE 1 I.r. spectra (in toluene solution) of complexes: (*a*), (I; X = 2-Cl); (*b*), (III; X = 2-Cl, L = PPh_3); and (*c*), (IV; X = 2-Cl, L = PPh_3)

The kinetic equations adopted to treat the data were

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[1] G. Cardaci, S. M. Murgia, and A. Foffani, *J. Organometallic Chem.*, 1972, **37**, C11.

[2] G. Cardaci and A. Foffani, *J.C.S. Dalton*, 1974, 1808.

[3] G. Cardaci and S. M. Murgia, *J. Organometallic Chem.*, 1970, **25**, 483.

[4] P. S. Braterman, *J.C.S. Chem. Comm.*, 1972, 761; P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, 1973, **2**, 271.

[5] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 705.

[6] J. Powell and A. W. L. Chan, *J. Organometallic Chem.*, 1972, **35**, 203.

those previously reported.[7] The complex concentration was *ca.* 10^{-2}M when the i.r. technique was adopted, *ca.*

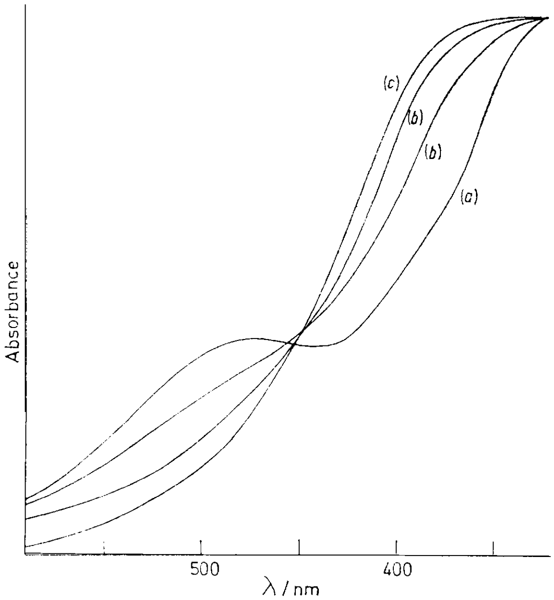

FIGURE 2 U.v. spectra (toluene solution): (*a*) (I; X = 2-Cl), (*b*), recorded during formation of (III); (*c*) [III; X = 2-Cl; L = $P(OEt)_3$]

2 × 10^{-3}M when the u.v. one was used.* At least a tenfold excess of phosphine ligand (over the complex concentration) was always present, to ensure pseudo-first-order kinetics.

RESULTS AND DISCUSSION

(a) *Complexes* (I; X = 1-Me *or* -Ph, *and* 2-Me).—The two 1-substituted complexes reacted with phosphine ligands just as the unsubstituted one,[3] *i.e. via* an associative mechanism involving second-order kinetics, first-order with respect to both the substrate and the entering-ligand concentrations (Table 1). The 2-Me complex reacted similarly with $P(OEt)_3$. However, its reaction with PPh_3 showed (Table 2) that the experimental pseudo-first-order rate constant (k_{obs}) depended on the ligand concentration according to $k_{obs} = k_1 + k_2[L]$. This reflects the occurrence of parallel dissociative and associative mechanisms with rate constants k_1 and k_2. The presence of the dissociative path is supported by values of the activation parameters (Table 8). A dissociation mechanism has been observed also for the corresponding reactions of $[(\eta\text{-}C_3H_5)Co(CO)_3]$ and its derivatives,[8] while a mixed mechanism, favoured by the presence of NO ligands, occurs in the series $[Ni(CO)_4]$, $[Co(CO)_3NO]$, and $[Fe(CO)_2(NO)_2]$.[7,9,10] For (I; X = 2-Me), the low value of k_2 allows one to see the

TABLE 1

Second-order rate constants (k_1) in toluene for the reaction: (I) + L ⟶ (II) + CO

X	L	θ_c/°C	k/l mol^{-1} s^{-1}
H	PPh_3 *	50	$9{\cdot}94 \times 10^{-5}$
	PBu^n_3 *	50	$6{\cdot}80 \times 10^{-3}$
	$P(OEt)_3$ *	50	$4{\cdot}77 \times 10^{-3}$
	$Ph_2PCH_2CH_2PPh_2$ *	50	$1{\cdot}59 \times 10^{-3}$
	$P\{(OCH_2)_3CMe\}$ *	50	$3{\cdot}66 \times 10^{-3}$
1-Me	PPh_3	50	$5{\cdot}1 \times 10^{-5}$
	$P(OEt)_3$	29·8	$8{\cdot}3 \times 10^{-4}$
	$P(OEt)_3$	50	$2{\cdot}65 \times 10^{-3}$
2-Me	PPh_3	50	$1{\cdot}31 \times 10^{-5}$
	PPh_3	60	$2{\cdot}91 \times 10^{-5}$
	$P(OEt)_3$	30	$1{\cdot}70 \times 10^{-4}$
	$P(OEt)_3$	50	$6{\cdot}90 \times 10^{-4}$
1-Ph	$P(OEt)_3$	25	$5{\cdot}23 \times 10^{-3}$
	$P(OEt)_3$	35	$1{\cdot}04 \times 10^{-2}$

* Values from ref. 1.

TABLE 2

Rate constants in toluene for the reaction: (I; X = 2-Me) + L ⟶ (II; X = 2-Me) + CO

L	θ_c/°C	[L]/M	10^6k_{obs}/ s^{-1}	10^4k/ l mol^{-1} s^{-1}
$P(OEt)_3$	50	0·070		6·70
	50	0·088		7·06
	50	0·107		6·73
	50	0·207		7·06
	30	0·499		1·63
	30	0·994		1·77
PPh_3	50	0·050	2·49	
	50	0·100	3·03	
	50	0·236	4·36	
	50	0·477	7·94	
	50	0·779	12·6	
	50	1·045	15·9	
	60	0·050	9·87	
	60	0·100	10·6	
	60	0·251	16·1	
	60	0·500	22·3	
	60	0·750	30·0	
	60	0·999	36·5	

TABLE 3

Second-order rate constants (k_2) in toluene for the reaction: (I) + L ⟶ (III)

X	L	θ_c/°C	10^3k_2/l mol^{-1} s^{-1}
1-Cl	PPh_3	30	0·431
	PPh_3	50	0·924
	PBu^n_3	10	20·0
	$P(OEt)_3$	10	3·27
	PPh_2Et	20	3·58
	PPh_2Et	30	6·50
	$P\{(OCH_2)_3CEt\}$	20	3·50
2-Cl	PPh_3	30	0·30
	PPh_3	50	1·23
	PBu^n_3	10	42·7
	$P(OEt)_3$	20	7·9
	$P(OEt)_3$	30	16·0
	PPh_2Et	20	11·0
	PPh_2Et	30	14·2
	$P\{(OCH_2)_3CEt\}$	10	5·14
2-Br	$P(OEt)_3$	0	0·53
	$P(OEt)_3$	20	3·01
1-CN	PPh_3	0	0·35
	PPh_3	20	1·68
	PPh_3	0	Very rapid

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* 1M = 1 mol dm^{-3}.

[7] G. Cardaci, A. Foffani, G. Distefano, and G. Innorta, *Inorg. Chim. Acta*, 1967, **1**, 340.

[8] R. F. Heck, *J. Amer. Chem. Soc.*, 1963, **85**, 657.

[9] E. M. Thorsteinson and F. Basolo, *J. Amer. Chem. Soc.*, 1966, **88**, 3929; D. E. Morris and F. Basolo, *ibid.*, 1968, **90**, 2531.

[10] L. S. Meriwether and M. L. Fiene, *J. Amer. Chem. Soc.*, 1959, **81**, 4200; G. Cardaci, S. M. Murgia, and G. Reichenbach, *Inorg. Chim. Acta*, 1970, **4**, 118; G. Cardaci and S. M. Murgia, *ibid.*, 1972, **6**, 222.

dissociative contribution which is masked for the other complexes.

(b) *Complexes* (I; X = 1-CN, 1- *or* 2-Cl, *and* 2-Br).—Spectroscopic evidence [1,2] shows that these complexes react with phosphine ligands to give five-co-ordinate σ-allyl complexes, (III), which then rearrange to 1-σ,2—3-η-allyl complexes, (IV). The results in Tables 3 and 8 indicate second-order kinetics of formation for the complexes (III), first-order with respect to both the substrate and the entering-ligand concentrations; values of the activation parameters correspond to an associative mechanism. The subsequent rearrangement to complexes (IV) is first order, depending only on the concentration of (III). The kinetic information in Tables 4 and **7**, and the stoicheiometry of the reactions, points to an associative mechanism with intramolecular chelation. The overall reaction scheme is as in equation (1).

TABLE 4

First-order rate constants (k_1) in toluene for the reaction: (III) ⟶ (IV) + CO

X	L	θ_c/°C	10^4k_1/s^{-1}
1-Cl	PPh_3	30	0·402
	PBu^n_3	30	1·04
	PBu^n_3	40	3·28
	PBu^n_3	50	10·30
	$P(OEt)_3$	20	0·88
	$P(OEt)_3$	30	2·53
	$P(OEt)_3$	40	7·20
	PPh_2Et	20	0·29
	PPh_2Et	30	1·00
	$P\{(OCH_2)_3CEt\}$	30	18·10
2-Cl	PPh_3	40	0·46
	PPh_3	50	1·90
	PBu^n_3	30	0·10
	PBu^n_3	40	0·46
	PBu^n_3	50	1·57
	$P(OEt)_3$	30	0·33
	$P(OEt)_3$	40	0·95
	PPh_2Et	30	0·16
	PPh_2Et	40	0·65
	$P\{(OCH_2)_3CEt\}$	30	5·01
2-Br	$P(OEt)_3$	20	0·22
	$P(OEt)_3$	30	0·61
1-CN	PPh_3	20	0·17
	PPh_3	30	0·62
	$P(OEt)_3$	0	0·29
	$P(OEt)_3$	20	3·38

$$\underset{\text{(I)}}{[(\eta\text{-}C_3H_4X)Fe(CO)_2NO]} + L \xrightarrow{k_2} \underset{\text{(III)}}{[(\sigma\text{-}C_3H_4X)Fe(CO)_2(NO)L]} \xrightarrow{k_1} \underset{\text{(IV)}}{[(\sigma,\eta\text{-}C_3H_4X)Fe(CO)(NO)L]} + CO \quad (1)$$

(c) *Influence of the Nature of the Entering Ligand on the Rate of Formation of Complexes* (III).—Contrary to what is usually observed for substitution reactions of carbonyl complexes, the rate of this reaction does not depend solely on the basicity of the entering ligand [9] [expressed as the Δ(h.n.p.) value [11] of the ligand].* In fact, log k_2 varied linearly with Δ(h.n.p.) (Figure 3) only in the case of the phosphine ligands; the phosphites deviated remarkably from the plot, showing higher rates. The phosphite ligands differ from the phosphines in having stronger π-bonding ability,[12] which probably affects the rate of reaction. A greater π-bonding contribution to the Fe–L bond should stabilize the activated complex through which (III) is formed. This was foreseen by the theory of Chatt and Shaw [5] on the stabilization of σ-allyl complexes, and is in accord with kinetic results for substitution reactions on the parent complex (I; X = H) (see Figure 4). The anomalous behaviour of the phosphites, attributed in that case to their particular steric hindrance, should be reinterpreted in terms of these new observations.

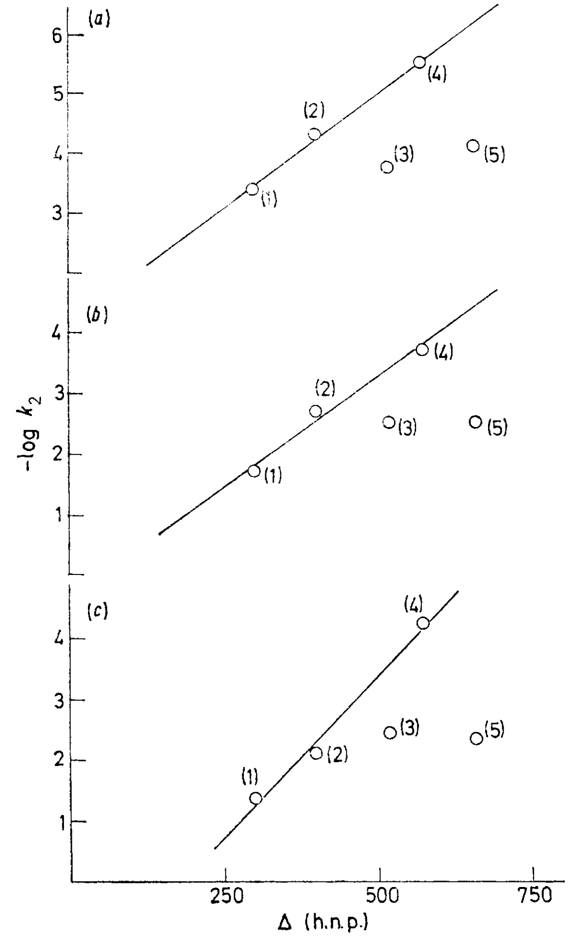

FIGURE 3 Plots of $-\log k_2$ against Δ(h.n.p.) for the reactions (I) + L ⟶ (III) with X = H (*a*), 1-Cl (*b*), and 2-Cl (*c*) at 10 °C. L = PBu^n_3 (1), PPh_2Et (2), $P(OEt)_3$ (3), PPh_3 (4), and $P\{(OCH_2)_3CEt\}$ (5)

The influence of the entering ligand was similar for (I; X = H) as for the substituted-allyl complexes. This is apparent from the good linearity of the plots in Figure 4, which correspond to rate constant values in

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* Δ(h.n.p.) = Half-neutralization potential referred to that of diphenylguanidine in nitromethane.

[11] C. A. Streuli, *Analyt. Chem.*, 1960, **32**, 985.

[12] W. D. Horrocks, jun., and R. Craig Taylor, *Inorg. Chem.*, 1963, **2**, 723.

Table 6 (which were estimated from activation parameters). It is inferred that even the complexes which do not reveal analytically the formation of (III) during ligand substitution do follow the above mechanism, possibly with $k_1 \gg k_2[\mathrm{L}]$ so as to preclude detection of (III).

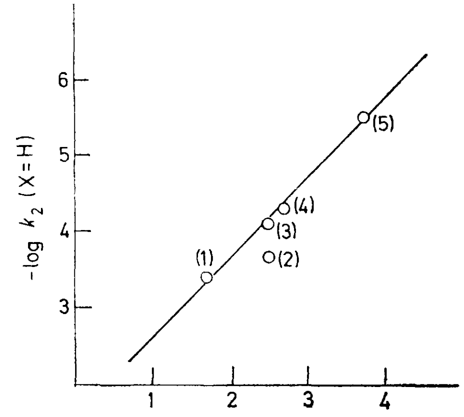

FIGURE 4 Plot of $-\log k_2$ for the reactions (I; X = H) + L $\longrightarrow$ (II; X = H) + CO against $-\log k_2$ for (I; X = 1-Cl) + L $\longrightarrow$ (III; X = 1-Cl) at 50 °C. L = $\mathrm{PBu^n_3}$ (1), $\mathrm{P(OEt)_3}$ (2), $\mathrm{P\{(OCH_2)_3CEt\}}$ (3), $\mathrm{PPh_2Et}$ (4), and $\mathrm{PPh_3}$ (5)

(d) *Influence of the Ligand* L *on the Rate of the Chelation Reaction.*—Figure 5 shows that for the first-order process of intramolecular chelation, (III) $\longrightarrow$ (IV), particularly studied in the 1- and 2-Cl derivatives, increased basicity of the L ligand reduces the rate of chelation; this could be due to a higher charge density on the central metal atom. The ligand $\mathrm{PPh_3}$ deviates remarkably from the plot, showing a lower rate than expected from its basicity; this may be due to the high steric hindrance of the ligand, which destabilizes the six-co-ordinate activated complex of the chelation process.

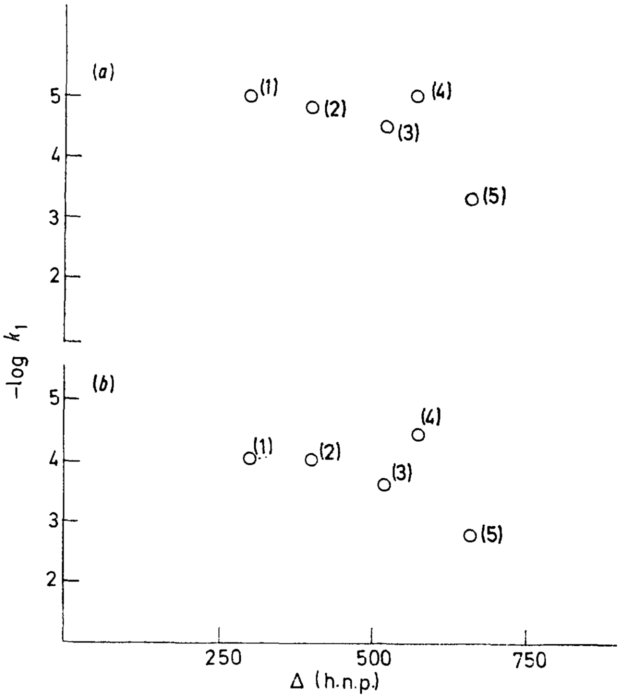

FIGURE 5 Plots of $-\log k$ against Δ(h.n.p.) for the reaction (III) $\longrightarrow$ (IV) + CO with (*a*) X = 2-Cl, (*b*) X = 1-Cl at 30 °C. L = $\mathrm{PBu^n_3}$ (1), $\mathrm{PPh_2Et}$ (2), $\mathrm{P(OEt)_3}$ (3), $\mathrm{PPh_3}$ (4), and $\mathrm{P\{(OCH_2)_3CEt\}}$ (5)

TABLE 5

Pseudo-first-order rate constants (k_{obs}) in toluene for the reaction: (III) $\longrightarrow$ (IV) or (V)

X	θ_c/°C	$[\mathrm{P(OEt)_3}]$/M	$10^4 k_{\mathrm{obs}}/\mathrm{s^{-1}}$
2-Cl	30	0·026	0·36
	30	0·049	0·37
	30	0·102	0·45
	30	0·252	0·51
	30	0·498	0·81
	30	0·749	1·05
	40	0·055	1·08
	40	0·252	1·50
	40	0·507	2·05
1-Cl	20	0·126	1·03
	20	0·350	1·22
	20	0·449	1·37
	20	0·657	1·65
	30	0·116	2·98
	30	0·313	3·66
	30	0·474	4·07
	30	0·686	4·70
	40	0·080	7·66
	40	0·210	9·14
	40	0·358	10·7
	40	0·558	12·2
	40	0·660	13·0
2-Br	20	0·143	0·19
	20	0·210	0·29
	20	0·457	0·43
	20	0·586	0·45
	20	0·610	0·49
	30	0·120	0·64
	30	0·218	0·78
	30	0·420	0·93
	30	0·770	1·18
1-CN	0	0·279	0·28
	0	0·403	0·30
	0	0·617	0·28
	20	0·164	3·40
	20	0·300	3·37
	20	0·465	3·37
	20	0·667	3·45

* Values of k_2/l $\mathrm{mol^{-1}\,s^{-1}}$ (θ_c/°C) obtained by extrapolation (Figure 6) are: (X = 2-Cl) $9·47 \times 10^{-5}$ (30), $2·09 \times 10^{-5}$ (40); (X = 1-Cl) $11·7 \times 10^{-5}$ (20), $35·3 \times 10^{-5}$ (30), $91·3 \times 10^{-5}$ (40); (X = 2-Br) $4·25 \times 10^{-5}$ (20), $7·43 \times 10^{-5}$ (30); (X = 1-CN) $\simeq 0$.

(e) *Influence of the* X *Substituent on the Rate of Formation of Complex* (III) *and on the Rate of Chelation.*—On the assumption that the 1-substituted complexes are all in the same isomeric form (*syn*- or *anti*-),[2,13] Tables 1, 3, and 6 show that the position of the X substituent changes the rate of formation of complex (III), but only by a factor of two or three, and not always in the same direction; the main factor affecting the rate should be, therefore, the electronic properties of the entering ligand [see (*c*) above]. For the same series of isomers (1- or

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[13] W. R. McClellan, H. H. Cripps, E. L. Muetterties, and B. W. Howk, *J. Amer. Chem. Soc.*, 1961, **83**, 1601.

2-substituted), electron-donating substituents lowered the rate, for the increased charge density on the central metal atom opposes nucleophilic attack of the ligand.

Table 4 shows that electron-attracting substituents favour intramolecular chelation, particularly when in position 1; the opposing action of different factors makes it difficult to rationalize this effect.

(f) CO *Insertion Reactions with Phosphite Ligands.*—It has been observed[2] that the reaction between (III; X = 1- or 2-Cl, and 2-Br) and $P(OR)_3$ (R = Me or Et) also gives but-3-enoyl complexes, (V). These species occur as side products during the formation of complexes (IV) from the intermediates (III). The data in Table 5 indicate that in these cases a two-term rate law is operative, giving pseudo-first-order rate constants like those reported in (*a*) above. This behaviour can be explained in terms of the occurrence of two parallel reaction paths, k_1 in equation (1) and k_3 in (2). This mechanism applies only with the phosphite derivatives, presumably due to the combined action of the nucleophilic and

$$[(\sigma\text{-}C_3H_4X)Fe(CO)_2(NO)L] \xrightarrow[L]{k_3} [(\sigma\text{-}XC_3H_4CO)Fe(CO)(NO)L_2] \quad (2)$$

π-acceptor character of these ligands, for both factors favour the disubstitution reaction. In fact, the π-contribution to the Fe–L bond in complexes (III) destabilizes the Fe–CO bonds, and the basicity of the entering ligand L increases the rate of disubstitution. The present data do not afford an indication of the mechanism of the insertion reaction.

TABLE 6

Second-order rate constants (k_2/l mol^{-1} s^{-1}) at 10 °C in toluene for the reaction: (I) + L ⟶ (III)

X	H *	2-Cl	1-Cl
L	10^5k_2	10^3k_2	10^3k_2
PPh_2Et	5·40 †,‡	8·36 †	1·92 †
$P(OEt)_3$	22·0 †	4·05 †	3·27 †
PPh_3	0·33 †	0·06 †	0·19 †
PBu^n_3	42·3 †	42·7	20·0
$P\{(OCH_2)_3CEt\}$	8·17 †	5·14	3·50 §

* A few values of the activation parameters, used to calculate the rate constants, were obtained from ref. 1; the remainder were measured in this work. † Calculated from the activation parameters. ‡ Referred to the $Ph_2PCH_2CH_2PPh_2$ ligand. § At 20 °C.

TABLE 7

First-order rate constants (k_1) at 30 °C in toluene for the reaction: (III) ⟶ (IV) + CO

X	1-Cl	2-Cl
L	10^4k_1/s^{-1}	10^5k_1/s^{-1}
$P(OEt)_3$	2·53	3·30 *
PBu^n_3	1·04	1·00
PPh_3	0·403	1·06 *
PPh_2Et	0·996	1·61
$P\{(OCH_2)_3CEt\}$	18·1	50·1 *

* Calculated from the activation parameters.

TABLE 8

Activation parameters

		k_1		k_2	
X	L	$\Delta H^\ddagger$/ kcal mol^{-1}	$\Delta S^\ddagger$/cal K^{-1} mol^{-1}	$\Delta H^\ddagger$/ kcal mol^{-1}	$\Delta S^\ddagger$/cal K^{-1} mol^{-1}
(*a*) (I) + L ⟶ (IV) + CO					
H	$P\{(OCH_2)_3CEt\}$			21·2	−5
	PBu^n_3			6·6	−53
2-Me	$P(OEt)_3$			13·6	−33
	PPh_3	34·4	+19	17	−30
1-Ph	$P(OEt)_3$			11·6	−32
(*b*) (I) + L ⟶ (III)					
2-Cl	PPh_3			13·6	−32
	PPh_2Et			4·5	−55
	$P(OEt)_3$			12·5	−27
1-Cl	PPh_3			7·2	−52
	PPh_2Et			10·7	−35
2-Br	$P(OEt)_3$			13·1	−27
(*c*) (III) ⟶ (IV) + CO					
2-Cl	PPh_3	28·1	+9		
	$P(OEt)_3$	19·9	−15	14·9 *	−30 *
	$P\{(OCH_2)_3CEt\}$	19·0	−13		
	PBu^n_3	26·6	+3		
	PPh_2Et	26·4	+5		
1-Cl	PBu^n_3	22·2	−6		
	PPh_2Et	26·4	+5		
	$P(OEt)_3$	19·1	−14	18·9 *	−14 *
2-Br	$P(OEt)_3$	17·7	−21	9·8 *	−47 *
1-CN	PPh_3	22·5	−6		
	$P(OEt)_3$	19·6	−9		

* Referred to the disubstitution reaction (2).

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