Kinetics and Mechanism of Substitution of Olefinic Ligands by Carbon Monoxide in Tetracarbonyl-π-olefiniron Complexes

By **G. Cardaci,*** and **V. Narciso,** Institute of Physical Chemistry, University of Perugia, 06100 Perugia, Italy

The mechanism of the reaction $Fe(CO)_4(CH_2{=}CHX) + CO \longrightarrow Fe(CO)_5 + CH_2{=}CHX$ (X = OEt, Bu, Ph, CO_2Me, and CN) has been studied in toluene. The reaction mode has been found to be dissociative with intermediate formation of $Fe(CO)_4$; an appreciable mass law retardation effect of the olefinic ligand has been found. The thermal stability of the olefinic complexes is correlated with the electron-withdrawing power of the substituent X. The relative order of thermodynamic stability of the complexes has been deduced from the mass law retardation effects of the olefinic ligands.

THE mechanism of substitution of olefinic ligands in square-planar complexes[1] is associative whilst in pseudo-octahedral complexes[2] it is dissociative. This behaviour is also observed for other substitution reactions in square-planar and octahedral complexes[3] and is due to an increase in steric hindrance with increasing co-ordination number.

In this work the substitution of some olefinic ligands by carbon monoxide in trigonal-bipyramidal[4] $(CH_2{=}CHX)Fe(CO)_4$ complexes is studied in order to observe what influence five-co-ordination may have on the substitution mechanism. The effect of the substituent X of the olefinic group on the rate of substitution is also investigated in order to obtain information on the factors affecting the stability of olefinic complexes.

$$(CH_2{=}CHX)Fe(CO)_4 + CO \longrightarrow Fe(CO)_5 + CH_2{=}CHX \qquad (1)$$

$$(X = OEt, Ph, Bu, CHO, CO_2Me, \text{and } CN)$$

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EXPERIMENTAL

The olefinic complexes were prepared by reaction of $Fe_2(CO)_9$ and the ligand.[5-7] This method was also adopted for the hex-1-ene complex, not previously described. Ethyl vinyl ether and hex-1-ene complexes were purified by distillation, the remainder by crystallization. Complexes were characterized by their CO stretching frequencies and by C, H, and N analyses.* The values observed for the hex-1-ene complex are 2082, 1992, and 1968 cm^{-1} (liquid) (Found: C, 47·1; H, 4·9. Calc. for $C_{10}H_{12}FeO_4$: C, 47·55; H, 4·8%).

The acrylaldehyde derivative does not react with CO up to 50 °C. At higher temperatures the reaction proceeds according to equations (2) and (3) [8] as well, possibly, as that of (1).

$$2(CH_2{=}CHCHO)Fe(CO)_4 \longrightarrow (CH_2{=}CHCHO)Fe(CO)_3 + CH_2{=}CHCHO + Fe(CO)_5 \quad (2)$$

$$(CH_2{=}CHCHO)Fe(CO)_3 + 2CO \longrightarrow CH_2{=}CHCHO + Fe(CO)_5 \quad (3)$$

The kinetic runs were performed in the dark in deaerated toluene, previously distilled over Na. The reaction vessel used was a capped thermostatted flask [9] from which the solution was withdrawn by a syringe at different intervals. The solution was saturated with CO, prepared and purified according to ref. 10. During the kinetic runs the reaction vessel was connected to a CO reservoir (a thermostatted constant-pressure gas burette) to maintain constant CO pressure. A partial pressure of CO lower than atmospheric was obtained by dilution of CO with N_2 using Mohr bottles to measure gas volumes. The solution was stirred magnetically during the reaction. The CO concentration in toluene at various temperatures and at atmospheric pressure was obtained by interpolating literature values [10-12] and assuming Henry's law when dilution with N_2 was carried out.

Since the CO partial pressure is constant during the reaction, the kinetic runs were performed under pseudo-first-order conditions. The equations used to obtain the rate constants are reported in ref. 13. The concentration of the olefinic complexes was measured by the disappearance of the CO stretching mode at its highest frequency. It is not possible to observe the formation of $Fe(CO)_5$ because its CO bands are superimposed on those of the olefinic complexes. The decomposition of the olefinic complexes in the presence of CO may be neglected because, on completion of reaction, the concentration of $Fe(CO)_5$ corresponds to that of the olefinic complexes. In the absence of CO, the reaction product is $Fe_3(CO)_{12}$, as observed previously.[14] Generally, an excess of olefinic ligand was used to avoid a change of its concentration, during the kinetic runs, arising from the ligand liberated during reaction (1). Because of its high volatility vinyl ether was added to the reaction vessel by a microsyringe.

The measurements were recorded in 0·5 mm NaCl cells on Perkin-elmer 337 and 257 i.r. spectrophotometers. The temperatures were in the range 30—71·2 °C depending on the olefinic ligand. The reactions were always carried out to at least 50% change.

RESULTS

The pseudo-first-order rate constants (k) in toluene, for various concentrations of olefinic ligand are collected in

TABLE 1

Pseudo-first-order rate constants (k) in toluene for the $(CH_2{=}CHPh)Fe(CO)_4$ complex

t/°C	10^2[L]/M	10^5k/s^{-1}
30·0	0	0·89
40·0	0	4·00
	0·47	2·68
	0·51	2·31
	0·97	1·89
	1·34	1·48
	1·77	1·39
	2·55	0·93
	4·20	0·69
45·0	0	8·00
	0·77	5·22
	1·19	4·12
	1·90	3·28
	2·42	2·64
	4·90	1·70
50·0	0	16·00
	0·77	9·10
	1·19	8·20
	1·99	6·30
	2·42	5·10
	2·85	4·60
	6·37	2·60

TABLE 2

Pseudo-first-order rate constants (k) for the $(CH_2{=}CHOEt)Fe(CO)_4$ complex in toluene

t/°C	10^2[L]/M	10^5k/s^{-1}
35·0	0	15·20
	2·51	4·90
	5·02	2·90
	7·53	1·90
	10·40	1·50
40·0	0	24·50
	2·51	8·55
	5·02	5·52
	7·53	3·78
	10·40	2·61
45·0	0	38·80
	2·51	13·90
	5·02	8·80
	7·53	6·30
	10·40	4·70

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* Analysis of $(CH_2{=}CHX)Fe(CO)_4$ complexes.

	Calc./%			Found/%		
X	C	H	N	C	H	N
OEt	40·0	3·35		39·5	3·5	
Ph	53·0	2·95		53·2	3·2	
CO_2Me	37·85	2·40		37·3	2·6	
CN	38·05	1·35	6·35	38·5	1·6	6·0
Bu^t	47·55	4·80		47·1	4·9	
CHO	37·55	1·80		37·8	1·9	

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TABLE 3

Pseudo-first-order rate constants (k) for the $(CH_2{=}CHBu)Fe(CO)_4$ complex in toluene

t/°C	10^2[L]/M	10^5k/s^{-1}
45·0		6·66 [a]
	1·02	2·88
	1·98	1·87
	3·09	1·32
	3·93	1·08
50·0		13·15 [a]
	1·18	6·23
	1·47	4·81
	1·88	4·34
	2·94	3·10
	3·37	2·63
	4·11	2·43
60·0		41·60 [a]
	1·14	22·40
	2·04	17·70
	3·00	13·60
	4·09	10·90

[a] Extrapolated values from equation (6).

TABLE 4

Pseudo-first-order rate constants (k) for the $(CH_2{=}CHCN)Fe(CO)_4$ complex in toluene

t/°C	10^2[L]/M	10^5k/s^{-1}
60·0	0	0·94
65·0	0	1·90
71·2	0	4·98
	1·25	4·42
	3·58	3·63
	5·70	3·13
	10·00	2·42

TABLE 5

Pseudo-first-order rate constants (k) for the $(CH_2{=}CHCO_2Me)Fe(CO)_4$ complex in toluene

t/°C	10^2[L]/M	10^5k/s^{-1}
59·8	0	1·26
64·2	0	2·25
71·2		5·13 [a]
	1·32	2·45
	2·09	1·84
	2·89	1·45
	3·05	1·42

[a] Extrapolated value from equation (6).

Tables 1—5. Those for styrene, at 40 °C in toluene with [styrene] = 5×10^{-3}M and a different partial pressure of CO, are listed in Table 6.

TABLE 6

Pseudo-first-order rate constants (k) for the $(CH_2{=}CHPh)Fe(CO)_4$ complex in toluene at 40·0 °C

10^3[L]/M	P_{CO}/atm.	10^5k/s^{-1}
5·0	1	2·31
5·0	0·50	2·30
5·0	0·33	1·72
5·0	0·25	1·50

TABLE 7

Kinetic and equilibrium data at various temperatures for the $(CH_2{=}CHX)Fe(CO)_4$ complexes in toluene

X	t/°C	k_1/s^{-1}	tanα	$k_{-1} : k_2$	K_e [b]
Ph	30	$8·85 \times 10^{-6}$			
	40	$3·70 \times 10^{-5}$	$2·70 \times 10^{6}$	0·675	
	45	$8·00 \times 10^{-5}$	$1·16 \times 10^{6}$	0·555	1
	50	$1·60 \times 10^{-4}$	$0·50 \times 10^{6}$	0·461	
	71·2	$2·24 \times 10^{-3}$ [a]	$1·95 \times 10^{4}$ [a]	0·226	
OEt	35	$1·52 \times 10^{-4}$	$0·53 \times 10^{6}$	0·600	
	40	$2·45 \times 10^{-4}$	$0·32 \times 10^{6}$	0·491	
	45	$3·88 \times 10^{-4}$	$0·17 \times 10^{6}$	0·401	6·7
	71·2			0·157 [a]	
Bu	45	$0·67 \times 10^{-4}$	$1·95 \times 10^{6}$	0·776	0·62
	50	$1·32 \times 10^{-4}$	$0·83 \times 10^{6}$	0·631	
	60	$4·16 \times 10^{-4}$	$0·17 \times 10^{6}$	0·399	
	71·2			0·254 [a]	
CN	45	$8·95 \times 10^{-7}$ [a]			
	60·0	$0·94 \times 10^{-5}$			
	65	$1·90 \times 10^{-5}$			
	71·2	$4·98 \times 10^{-5}$	$2·10 \times 10^{5}$	0·054	$9·2 \times 10^{-2}$
CO_2Me	45	$6·08 \times 10^{-6}$ [a]			
	59·6	$1·26 \times 10^{-5}$			
	64·2	$2·25 \times 10^{-5}$			
	71·2	$5·13 \times 10^{-5}$	$1·68 \times 10^{6}$	0·445	$8·7 \times 10^{-3}$

[a] Values calculated from the thermal parameters. [b] Equilibrium constants calculated for reaction (10), taking ligand L_2 = styrene.

First-order rate constants (k_1), the mass law retardation ratio $k_{-1} : k_2$ [referred to the mechanism in equation (4)], and equilibrium constants of the olefinic exchange reactions are collected in Table 7. Thermal parameters of the dissociative step, the relative free energy for the various ligands ($\Delta G_1 - \Delta G_2$), and thermal parameters calculated from the mass law retardation ratios are listed in Table 8.

DISCUSSION

Reaction Mechanism.—The kinetic parameters, collected in Tables 1—6, show that the experimental rate constants (k) are dependent on both CO and olefinic ligand concentrations. Since reaction (1) is irreversible, an explanation of the influence of the olefinic ligand can be found in the formation of an intermediate, $Fe(CO)_4$,

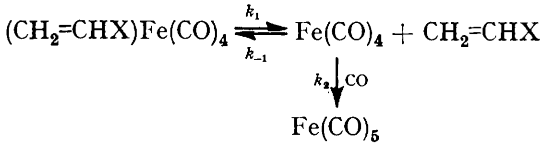
TABLE 8

Thermal parameters and free-energy values for $(CH_2{=}CHX)Fe(CO)_4$ complexes at 45 °C

X	$\Delta E^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}$/kcal mol^{-1}	ΔG_x [a]/kcal mol^{-1}	$\Delta(E_2^{\ddagger} - E_{-1}^{\ddagger})$/kcal mol^{-1}	$\Delta(S_2^{\ddagger} - S_{-1}^{\ddagger})$/cal K^{-1} mol^{-1}	$-(\Delta G_1 - \Delta G_2)$ [b]/kcal mol^{-1}
Ph	28·0 ± 0·3	+9 ± 1	24·6	0	7·7 ± 1·0	25 ± 3	0
OEt	18·3 ± 0·3	−19 ± 1	23·7	+0·3	7·8 ± 1·0	26 ± 3	+1·2
Bu	25·0 ± 0·3	−1 ± 1	24·7	−0·2	9·3 ± 1·0	33 ± 3	−0·3
CN [c]	33·2 ± 0·3	+16 ± 1	27·0	+1·0			−1·6
CO_2Me [c]	28·6 ± 0·3	+3 ± 1	27·0	−0·4			−3·2

[a] Values reported are positive if the position of the activated complex is higher than that of the styrene complex; if this is not the case then they are negative. [b] Free-energy values for reaction (10), taking ligand L_2 = styrene. [c] Values calculated at 71·2 °C.

in equilibrium with the olefinic complexes [mechanism (4)].



$$(CH_2{=}CHX)Fe(CO)_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(CO)_4 + CH_2{=}CHX \qquad Fe(CO)_4 \xrightarrow[k_2]{CO} Fe(CO)_5 \tag{4}$$

The intermediate $Fe(CO)_4$ is not observed experimentally; using the steady-state approximation, the following equation for the reaction rate is obtained, where the

$$\text{Rate} = \frac{k_1k_2[CO]}{k_{-1}[L] + k_2[CO]}[C] \tag{5}$$

rate constant subscripts refer to mechanism (4), [L] is the ligand concentration, and [C] is the complex concentration. Since the kinetic runs follow a pseudo-first-order rate law, Rate $= k$[C], the value of k is given by equation (6) [*cf.* equation (5)]. Thus at constant

$$k = \frac{k_1k_2[CO]}{k_{-1}[L] + k_2[CO]} \quad \text{or} \quad \frac{1}{k} = \frac{k_{-1}[L]}{k_1k_2[CO]} + \frac{1}{k_1} \tag{6}$$

CO pressure a plot of $1/k$ against [L] should be linear, with a slope of $k_{-1}/k_1k_2[CO]$ and an intercept of $1/k_1$.

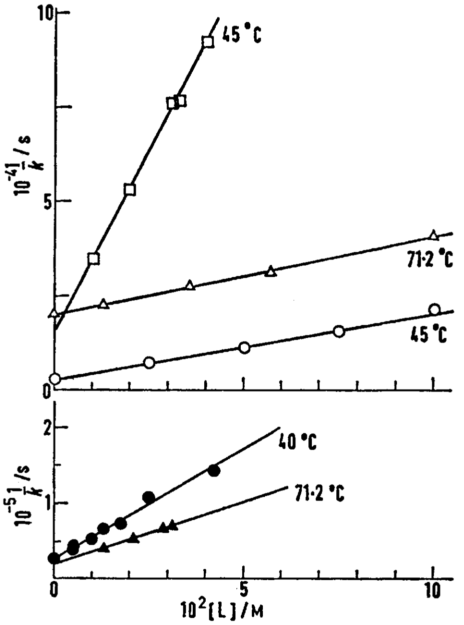


FIGURE 1 Plots of $1/k$ against [L] for the olefinic complexes $(CH_2{=}CHX)Fe(CO)_4$ where X = Bu, (□); CN, (△); OEt, (○); Ph, (●); and CO_2Me, (▲)

Figure 1 shows the plots obtained for the various complexes using this procedure. At constant [L] and different concentrations of CO, the plot of $1/k$ against 1/[CO] should also be linear with a slope of $k_{-1}[L]/k_1k_2$ and an intercept of $1/k_1$ (Figure 2). Values of k_1 and the ratio $k_{-1} : k_2$ obtained for styrene at 40 °C are $3{\cdot}7 \times 10^{-5}$ s^{-1} and 0·675 respectively (from Figure 1) and $3{\cdot}9 \times 10^{-5}$ s^{-1} and 0·634 (from Figure 2); individual values differ from one another by 5%.

In the absence of an excess of olefinic ligand, the reaction does not show any sensible mass law retardation effect, except for the hex-1-ene and methyl methacrylate ligands. The experimental values of k_1 (Table 7) agree with those extrapolated from Figures 1 and 2.

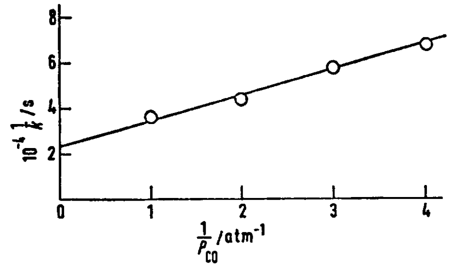


FIGURE 2 Plot of $1/k$ against $1/p_{CO}$ for the complex $(CH_2{=}CHPh)Fe(CO)_4$ at 40 °C

The formation of the intermediate $Fe(CO)_4$ is in agreement with the mechanism suggested for pseudo-octahedral and octahedral complexes.[2,15] In the absence of an excess of CO, formation of $Fe_3(CO)_{12}$ [14] from $Fe(CO)_4$ is easily understandable in the light of mechanism (4). Because of the formation of $Fe_3(CO)_{12}$ it is not possible to perform stability tests. However, in a large excess of the olefinic ligand, the formation of $Fe(CO)_5$ is very slow and the olefinic complexes are stable.

Kinetic measurements were performed at at least three different temperatures and plots of log k_1 against $1/T$ are linear. The Arrhenius activation energies and entropies are, except for the vinyl ether complex, in agreement with a dissociative mechanism (Table 8) for the first step of the reaction.[13] The plots of log k_{-1}/k_2 against $1/T$ are also linear; from the slopes it is possible to obtain the differences in thermal parameters for the reaction of the intermediate with CO and that with the olefinic ligand. The values are somewhat inaccurate (Table 8) but the linearity of the diagram is a further test of mechanism (4).

Substituent Effects.—The formation of $Fe(CO)_5$ is dependent on the competition reactions of $Fe(CO)_4$ with CO and the olefinic ligand. The rate constants may be compared and information obtained concerning substituent effects. Although it is not possible to obtain thermodynamic parameters from the kinetic data, owing to the irreversibility of the reaction studied, comparison of the kinetic data for different substituents proves interesting.

(*a*) *Comparative thermodynamic stability of the olefinic complexes and deduction of equilibrium constants for the olefinic exchange reactions.* Let $(\tan\alpha)_1 = \frac{k_{-1}(1)}{k_1(1)k_2[CO]}$ and $(\tan\alpha)_2 = \frac{k_{-1}(2)}{k_1(2)k_2[CO]}$ be the values of the slope of Figure 1

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[15] M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Amer. Chem. Soc.*, 1971, **93**, 6048.

for ligands L_1 and L_2, and K_1 and K_2 indicate the equilibrium constants for the reactions (7) and (8) respectively. Then the ratio of the slopes for ligands L_1

$$L_1Fe(CO)_4 \underset{k_{-1}(1)}{\overset{k_1(1)}{\rightleftharpoons}} L_1 + Fe(CO)_4 \qquad (7)$$

$$L_2Fe(CO)_4 \underset{k_{-1}(2)}{\overset{k_1(2)}{\rightleftharpoons}} L_2 + Fe(CO)_4 \qquad (8)$$

and L_2 leads to equation (9), where $\Delta G_1 - \Delta G_2$ gives a

$$\Delta G_1 - \Delta G_2 = 2{\cdot}3\ RT \log (\tan\alpha)_1/(\tan\alpha)_2 \qquad (9)$$

measure of the variation of the free energy of reaction (10). It is possible therefore to calculate values of the

$$L_1Fe(CO)_4 + L_2 \rightleftharpoons L_2Fe(CO)_4 + L_1 \qquad (10)$$

equilibrium constants of (10) (Table 7), taking L_2 = styrene.

(*b*) *Comparative energetic positions of the activated complexes for different olefinic ligands.* Referring to Figure 3, the following equation may be obtained, where $\Delta G_2^\ddagger$ and

$$(\Delta G_1 - \Delta G_2) + \Delta G_2^\ddagger = \Delta G_1^\ddagger + \Delta G_x \qquad (11)$$

$\Delta G_1^\ddagger$ are the free energies of activation for the first step of reaction (4) with ligands L_2 and L_1 respectively, and ΔG_x is the difference in energy position of the activated complexes for the two cases. Since $(\Delta G_1 - \Delta G_2)$ is calculated as mentioned in (*a*) and $\Delta G_2^\ddagger$ and $\Delta G_1^\ddagger$ are measured experimentally (Table 8), ΔG_x values for different substituents may be obtained and are collected in Table 8 for L_2 = styrene.

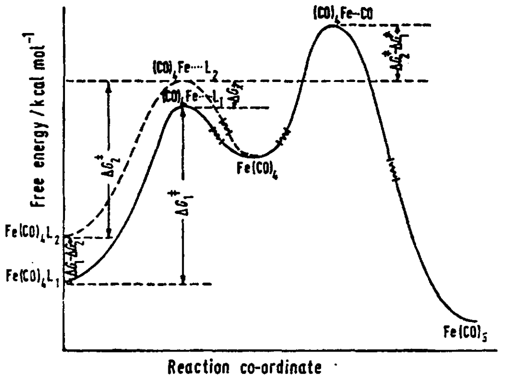

FIGURE 3 Plot of free energy against reaction co-ordinate for the reaction $LFe(CO)_4 + CO \longrightarrow Fe(CO)_5 + L$; L_1 and L_2 are two different olefinic ligands

The substituent X effects the substitution of $CH_2{=}CHX$ by CO, changing the rate constants k_1, the value of ΔG_x, the equilibrium constant of the ligand-exchange reaction (11), and finally the mass law retardation ratio $k_{-1} : k_2$.

A plot of log k_1 against the Hammett value σ_p is shown in Figure 4. The trend is linear, as observed previously for other complexes;[16] only the hex-1-ene complex departs from the straight line and the explanation of this behaviour is not clear. A linear trend is also observed in the plot of log k_1 against V, values for V * being reported in ref. 14. The thermal stability of the complexes is therefore affected predominantly by the acceptor strength of the substituent X.

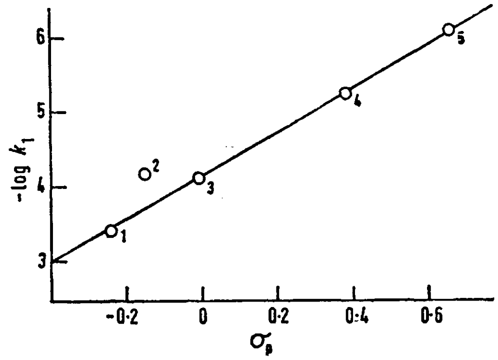

FIGURE 4 Plot of log k_1 against the Hammett value σ_p for the complexes $(CH_2{=}CHX)Fe(CO)_4$ in toluene at 45 °C. X = OEt, (1); Bu, (2); Ph, (3); CO_2Me, (4); and CN, (5)

The ΔG_x values, calculated as indicated in (*a*), are within the limits of experimental error for all the complexes studied (except for the ligand acrylonitrile). This means that the loosening of the π-olefin bond during the formation of the activated complex is so large that the substituent influence is experimentally negligible

The trend of the thermodynamic stability, indicated by the free-energy values of reaction (10), agrees with those for the V and σ_p Hammett values. No minimum value in the trend was observed, contrary to the situation found in ref. 17 for some olefinic Pt^{II} complexes. Therefore, in this case, the ligand acceptor strength stabilizes the metal olefinic bond because it lowers the energy of the π* antibonding orbital of the olefinic ligand, making the latter capable of accepting the *d* electron of the iron atom.

The influence of the substituent on the mass law retardation ratio $k_{-1} : k_2$ is small (Table 7). This is due to the low discriminating power of the intermediate $Fe(CO)_4$, which possesses a high reactivity towards the ligands. In accordance with this the activation energy of the reaction of $Fe(CO)_4$ with the olefinic ligands is very low as indicated in Figure 3.

We are indebted to Prof. U. Mazzucato for helpful criticism.

[2/714 *Received, 27th March,* 1972]

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* V = Acceptor strength of ligand L/donor strength of ligand L. This ratio is approximately equal to $I.P./(E_d - E_{\pi^*})$, where I.P. is the ionization potential of the π-donor ligand, E_d is the *d*-level energy of the highest occupied Fe states in $Fe(CO)_4$, and E_{π^*} is the energy of the antibonding π* state of the olefin.

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[17] John R. Joy and M. Orchin, *J. Amer. Chem. Soc.*, 1959, **81**, 305.