Mechanism of Formation of Chelated Tricarbonyliron Complexes of α,β-Unsaturated Schiff Bases from the corresponding Tetracarbonyliron Complexes: Factors affecting the Stability of the Trigonal-bipyramidal Complexes

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The chelation reaction of the complexes $[Fe(CO)_4\{N(C_6H_4X)=CH-CH=CHPh\}]$ (1) to form $[Fe(\eta\text{-}Ph-CH=CH-CH=N-C_6H_4X)(CO)_3]$ (2) (X = 4-Br, 4-OMe, and H) in the presence of excess Schiff base has been studied. The kinetics are first order in the complex concentration and the inverse of the rate constant varies linearly with the concentration of the Schiff base. The effect of CO on both the rate constants and the final reaction products has been studied. The results support a reaction mechanism similar to that proposed for the corresponding complexes of α,β-unsaturated aldehydes and ketones. The substitution reaction of (1) with PPh_3 has also been investigated. It proceeds *via* a dissociative mechanism. The observed effect of the substituents X on the rate constants allows the conclusion that in derivatives of tetracarbonyliron having a trigonal-bipyramidal structure the bond energy at the apical position depends mainly on the σ-bond strength, while that at the equatorial position depends on the amount of π-back bonding present.

THE mechanism of the chelation reaction of iron complexes of the type $[Fe(\eta\text{-}Ph-CH=CH-COR)(CO)_4]$ to give tricarbonyls has recently been studied.[1] The reaction does not proceed *via* an intramolecular chelation but by dissociation of the heterodiene ligand of the tetracarbonyl complex, with the formation of the intermediate $[Fe(CO)_4]$. This intermediate is responsible for the formation of the tricarbonyl complex, either *via* a further dissociation to $[Fe(CO)_3]$, as proposed by us,[1] or *via* intermediates of the type $[Fe_2(CO)_8]$ and $[Fe_2(CO)_7]$ as proposed by other workers.[2] This behaviour is in agreement with the mechanism of the simultaneous formation of $[Fe(CO)_4L]$ and $[Fe(CO)_3L_2]$ from various iron carbonyl complexes, which also proceeds *via* the formation of the intermediate $[Fe(CO)_4]$. The mechanism allows a rationalisation of the reactivity of iron carbonyl complexes.[3]

We now report an extension of this work to the formation of other heterodiene complexes of the type $[Fe(\eta\text{-}Ph-CH=CH-CH=N-C_6H_4X)(CO)_3]$, (2), from the tetracarbonyls $[Fe(CO)_4\{N(C_6H_4X)=CH-CH=CHPh\}]$, (1), with the aim of confirming the mechanism proposed previously.

EXPERIMENTAL

Complexes (1; X = Br, H, OMe, NMe_2, Me, F, or I) were prepared and purified as described previously.[4] Complexes (2) were obtained by literature methods.[4,5] The Schiff bases were prepared following standard literature methods,[4] using diethyl ether as solvent. Spectrophotometric measurements were made on a Perkin-Elmer IR 257 instrument, using 0.5-mm NaCl cells.

Kinetic Measurements.—The chelation reaction (1) was

$$[Fe(CO)_4\{N(C_6H_4X)=CH-CH=CHPh\}] \longrightarrow [Fe(\eta\text{-}Ph-CH=CH-CH=N-C_6H_4X)(CO)_3] + CO \quad (1)$$

followed in acetone (Carlo Erba, RS) which was thoroughly deaerated before use, and in the absence of light because of the photosensitivity of complex (1). Under these conditions, reaction (1) was quantitative and $[Fe(CO)_5]$ was not formed. In the presence of CO (p 1 atm),† $[Fe(CO)_5]$ was also formed. The concentration of $[Fe(CO)_5]$ decreased with increasing concentration of Schiff base and was negligible when the latter was *ca.* 1×10^{-2} mol dm^{-3} with X = Br. The relative amounts of $[Fe(CO)_5]$ and chelate complex (2) were determined by distilling at room temperature the solution obtained after 30% completion of reaction and collecting the distillate. During the distillation the product ratio was not affected.

The effect of varying the concentration of the Schiff base on the rate constants was examined. The kinetics were followed by observing the disappearance of the lower-frequency carbonyl-stretching band of (1) (1 945 cm^{-1} in acetone) and the appearance of the lower-frequency stretching band of (2) (1 995 cm^{-1} in acetone). Both bands obeyed Beer's law throughout the concentration range studied. First-order rate constants were obtained by plotting log (D_0/D) against t for the disappearance of (1) and $\log[D_\infty/(D_\infty - D)]$ against t for the disappearance of (2). Values obtained from the two sets of plots agreed to within 5% when the D_∞ for the second plot was calculated using Beer's law, instead of being determined experimentally, because of slight decomposition of complex (2) during the reaction.

The first-order rate constants refer to values obtained from the disappearance of the tetracarbonyl complex. The kinetics of the chelation reactions were also studied in the presence of a CO atmosphere. In this case the $[Fe(CO)_5]$: (2) ratio increased rapidly during the reaction. This behaviour is different from that found previously for α,β-unsaturated aldehydes.[1]

The reaction between (2) and CO was followed independently and it was observed that it proceeded with initial formation of complex (1), which then further reacted with CO to give $[Fe(CO)_5]$ [equation (2)]. Reaction (2) is

$$[Fe(\eta\text{-}Ph-CH=CH-CH=N-C_6H_4X)(CO)_3] + CO \longrightarrow [Fe(CO)_4\{N(C_6H_4X)=CH-CH=CH-Ph\}] + CO \longrightarrow [Fe(CO)_5] + N(C_6H_4X)=CH-CH=CH-Ph \quad (2)$$

similar to that observed for $[Fe(\eta\text{-}Ph-CH=CH-COR)(CO)_3]$

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† Throughout this paper: 1 atm = 101 325 Pa.

[1] G. Cardaci, *J. Amer. Chem. Soc.*, 1975, **97**, 1412.

[2] I. Fischler, K. Hildebrand, and E. Koerner Von Gustorf, *Angew. Chem. Internat. Edn.*, 1975, **14**, 54.

[3] G. Cardaci, *Inorg. Chem.*, 1974, **13**, 385, 2974.

[4] G. Cardaci and G. Bellachioma, *J.C.S. Dalton*, 1976, 1735.

[5] S. Otsuka, T. Yoshida, and A. Nakamura, *Inorg. Chem.*, 1967, **6**, 20.

with MPh_3 (M = P,[6,7] As,[7] or Sb[7,8]) which gives initial formation of the complexes $[Fe(\eta\text{-}PhCH{=}CHCOR)(CO)_3(MPh_3)]$ with a change in the heterodiene–iron bond from η^4 to η^2. Complexes (1), obtained in the course of reaction (2), were isolated, purified, and compared with authentic samples.[4] Since the second stage of reaction (2) is much slower than the first, the disappearance of complexes (2) in the initial part of the reaction was followed in several runs.

These reactions were performed in an apparatus[9] consisting of a thermostatted vessel fitted with a magnetic stirrer and connected to a thermostatted burette which maintained a constant CO pressure in the solution. Carbon mono-oxide was prepared as described in the literature,[10] and was first passed through a liquid-air trap to condense impurities.

Reaction of complexes (1) *with* PPh_3. Complexes (1) react with PPh_3 to give simultaneous formation of $[Fe(CO)_4(PPh_3)]$ and $[Fe(CO)_3(PPh_3)_2]$ [equation (3)] in which α is

$$[Fe(CO)_4\{N(C_6H_4X){=}CH{-}CH{=}CHPh\}] + (2-\alpha)PPh_3 \longrightarrow \alpha[Fe(CO)_4(PPh_3)] + (1-\alpha)[Fe(CO)_3(PPh_3)_2] + N(C_6H_4X){=}CH{-}CH{=}CH{-}Ph \quad (3)$$

the fraction of $[Fe(CO)_4(PPh_3)]$ per mol of complex (1). The ratio $\alpha : (1-\alpha)$ was determined from the ratio of the absorbances for the complexes $[Fe(CO)_4(PPh_3)]$ and $[Fe(CO)_3(PPh_3)_2]$ at the end of the reaction. First-order rate constants were measured from the increase in intensity of the carbonyl-stretching band (at 1 880 cm^{-1}) of $[Fe(CO)_3(PPh_3)_2]$. Neither the disappearance of complexes (1) nor the appearance of $[Fe(CO)_4(PPh_3)]$ could be followed because of overlap of the carbonyl-stretching bands of these complexes.

RESULTS AND DISCUSSION

Chelation Reaction of (1).—Table 1 lists the first-order rate constants (k) at 30 °C with changes in concentration of the Schiff base, L, and of CO. The rate constants decreased with increasing concentration of the Schiff bases. The linear plots of $1/k$ against [L] are shown in Figure 1. The intercepts of these plots ($X = H$, $k = 9.61 \times 10^{-5}$; $X = 4\text{-OMe}$, $k = 6.62 \times 10^{-5}$; $X = 4\text{-Br}$, $k = 13.30 \times 10^{-5}$ s^{-1}) are identical, within experimental error, to the first-order rate constants for reaction (3) ($X = H$, $k = 9.55 \times 10^{-5}$; $X = 4\text{-OMe}$, $k = 6.56 \times 10^{-5}$; $X = 4\text{-Br}$, $k = 13.51 \times 10^{-5}$ s^{-1}). The CO pressure had virtually no effect on the rate constants of reaction (1), in the very limited concentration range for which measurements were made. Rate constants for the reaction with X = 4-Br (Table 1, Figure 1) were the same as those measured in the absence of CO, within experimental error. At a CO pressure of 1 atm, the percentage of $[Fe(CO)_5]$ formed during the reaction was <60% and rapidly decreased to zero with increasing concentration of Schiff base. This behaviour is different from that for the corresponding reaction of complexes containing α,β-unsaturated aldehydes and ketones. With the latter complexes, under identical concentrations of CO and ligand, *ca.* 80—90% yields of $[Fe(CO)_5]$ are obtained which decrease less rapidly with increasing heterodiene ligand than with the present ligands.

TABLE 1

First-order rate constants for reaction (1) in acetone at 30 °C

X	$10^2[L]$ / mol dm^{-3}	10^5k[a] / s^{-1}
H[b]	0	9.63 ± 0.10
	1.25	7.03 ± 0.10
	2.50	5.39 ± 0.10
	4.50	4.47 ± 0.05
	6.00	3.54 ± 0.10
OMe[c]	0	6.56 ± 0.10
	0.82	6.48 ± 0.13
	0.95	6.38 ± 0.07
	1.38	5.96 ± 0.10
	2.66	5.75 ± 0.07
	4.01	5.94 ± 0.12
	6.28	5.11 ± 0.10
	8.02	4.79 ± 0.07
	9.84	4.76 ± 0.10
Br[d]	0	13.97 ± 0.25
	0.21	11.50 ± 0.23
	0.82	9.87 ± 0.15
	1.53	9.20 ± 0.18
	2.51	7.66 ± 0.18
	3.43	6.27 ± 0.12
	3.71	6.44 ± 0.15
	4.39	6.13 ± 0.12
	4.90	5.65 ± 0.07
	5.73	5.11 ± 0.11
	7.69	4.15 ± 0.09
	0	13.42 ± 0.30[e]
	0.71	9.10 ± 0.25[e]
	1.95	9.31 ± 0.10[e]
	4.15	6.70 ± 0.10[e]
	6.27	4.69 ± 0.07[e]

[a] Error limits are average deviations. [b] The initial complex concentration, $[complex]_0$, ranged from 2.5×10^{-3} to 4×10^{-3} mol dm^{-3}. [c] $[complex]_0 = 2 \times 10^{-3}$—$4 \times 10^{-3}$ mol dm^{-3}. [d] $[complex]_0 = 2.5 \times 10^{-3}$—$4.5 \times 10^{-3}$ mol dm^{-3}. [e] p_{CO} = 1 atm.

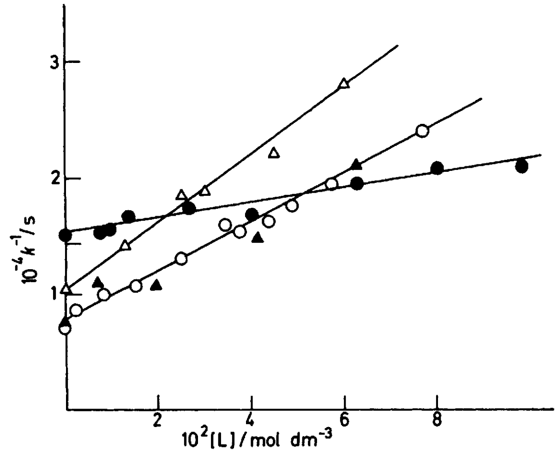

FIGURE 1 Plot of $1/k$ against [L] for reaction (1): X = H (△), OMe (●), Br (○), and Br(p_{CO} 1 atm) (▲)

The above results are in agreement with those obtained previously for complexes of α,β-unsaturated aldehydes and ketones,[1] apart from small differences due

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[6] A. Vessieres and A. Dixneuf, *Tetrahedron Letters*, 1974, 1499; *J. Organometallic Chem.*, 1976, **108**, C5.

[7] G. Cardaci and G. Concetti, *J. Organometallic Chem.*, 1974, **90**, 49.

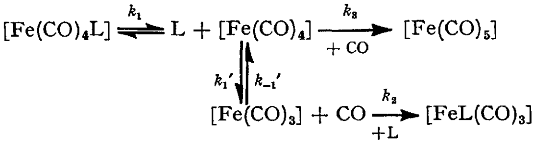
[8] G. Cardaci and S. Sorriso, *Inorg. Chem.*, 1976, **15**, 1842.

[9] G. Innorta, G. Reichenbach, and A. Foffani, *J. Organometallic Chem.*, 1970, **22**, 731.

[10] W. L. Gilliland and A. A. Blanchard, *Inorg. Synth.*, 1946, **2**, 81.

to the greater nucleophilicity of the Schiff bases. The following conclusions may be drawn: (*a*) there is a marked mass effect for the Schiff base, although for solubility reasons it was not possible to completely block the chelation reaction; (*b*) the CO pressure does not influence the rate constants; (*c*) the intercepts of Figure 1 correspond to the rate constants of reaction (3), which proceeds *via* a dissociative mechanism.[3,11]

The data confirm the mechanism proposed previously (Scheme 1). Applying the steady-state approximation



SCHEME 1

to the species $[Fe(CO)_4]$ and $[Fe(CO)_3]$ gives expression (4) for the first-order rate constant. This equation

$$\frac{1}{k} = \frac{1}{k_1} + \frac{k_{-1}k_2[L]^2 + k_{-1}k_{-1}'[CO][L]}{k_1k_2k_3[L][CO] + k_1k_1'k_2[L] + k_1k_{-1}'k_2[CO]^2} \quad (4)$$

reduces to (5) whether CO is present or not (because of the greater nucleophilicity of the Schiff base compared to that of CO), and is verified by the behaviour shown in Figure 1.

$$1/k = (1/k_1) + (k_{-1}/k_1k_1'[L]) \quad (5)$$

The mechanism proposed by other workers,[2] which predicts the formation of binuclear intermediates (Scheme 2), does not satisfy the kinetic results. According to Scheme 2 the chelation reaction should be second order with respect to the concentration of complex (1).

$$\begin{aligned}[Fe(CO)_4L] &\rightleftharpoons [Fe(CO)_4] + L\\ 2[Fe(CO)_4] &\rightleftharpoons [Fe_2(CO)_8]\\ [Fe_2(CO)_8] &\rightleftharpoons [Fe_2(CO)_7] + CO\\ [Fe_2(CO)_7] + L &\longrightarrow [FeL(CO)_3] + [Fe(CO)_4]\end{aligned}$$

SCHEME 2

The Substitution Reaction between (1) *and* PPh_3.—Table 2 lists first-order rate constants for reaction (3) for complexes (1) having different substituents in the benzene ring of the imide group. The effect of PPh_3 and the Schiff-base concentration on the rate constant was investigated for complex (1; X = Me). Variation of $[PPh_3]$ had no appreciable effect on the first-order rate constant, whilst increase in [L] caused a decrease in the rate constant. A plot of $1/k$ against [L] was linear, with an intercept corresponding to the rate constant measured in the absence of [L].

These results clearly indicate that the mechanism operating in this reaction is that proposed for the complexes $[Fe(\eta\text{-}CH_2{=}CHX)(CO)_4]$,[3,11] in which the rate-determining step is initial dissociation of the olefinic ligand with formation of the intermediate $[Fe(CO)_4]$. In the absence of Schiff base, the measured rate constant corresponds to k_1 in Scheme 1, as found experimentally. The gradient of the linear plot of k^{-1} *vs.* [L] allows calculation of the ratio $k_{-1} : k_3$, where k_{-1} refers to Scheme 1 and k_3 is a rate constant which takes into account the successive reactions of $[Fe(CO)_4]$. The value of the ratio is *ca.* 0.250 and indicates that the Schiff bases are less nucleophilic than PPh_3, as expected for the reactivity order for soft reaction centres.[12]

TABLE 2

First-order rate constants and $\alpha : (1 - \alpha)$ ratios for reaction (3) in acetone at 30 °C

X	$10^2[PPh_3]$ / mol dm^{-3}	10^2[L] / mol dm^{-3}	10^5k [a] / s^{-1}	$\alpha : (1 - \alpha)$	pK_b [b]
H	23.40		9.39 ±0.20	1.56	9.39
Br	27.30		13.98 ±0.31	2.80	10.12
I	20.40		17.63 ±0.42	2.52	10.21
F	23.50		9.66 ±0.15	1.90	9.38
OMe	20.10		6.61 ±0.12	0.85	8.66
NMe_2	25.30		10.92	0.54	7.41
	25.80		10.65	0.58	
	5.10		11.00	0.60	
Me	65.33		9.20	1.28	8.91
	34.74		8.81	1.26	
	8.78		9.39	1.21	
	5.07	3.95	8.50	1.01	
	5.04	7.01	7.41	0.83	
	5.07	9.98	6.81	0.75	
	5.04	12.48	5.75	0.54	

[a] Error limits are average deviations. [b] For the anilines from which the Schiff bases were obtained.

One difference compared to the reaction mechanism for $[Fe(\eta\text{-}CH_2{=}CHX)(CO)_4]$ complexes[3,11] is that in the present case the ratio $\alpha : (1 - \alpha)$ depends also on the nature of the substituent X as well as on the concentration of L (Table 1). Since the first step of the reaction is dissociative, the only explanation of this effect is that L reacts with the intermediates shown in Schemes 1 and 2. The above ratio $k_{-1} : k_3$ is in agreement with this possibility; it is higher than for the complexes $[Fe(\eta\text{-}CH_2{=}CHX)(CO)_4]$[3,11] [for which $\alpha : (1 - \alpha)$ remains constant]. Both an increase in the donor power of the substituent X (*i.e.* an increase in the nucleophilicity of the nitrogen atom) and an increase in the concentration of L lead to a decrease in $\alpha : (1 - \alpha)$. If this interpretation is correct, as the donor power of the nitrogen atom decreases, $\alpha : (1 - \alpha)$ should tend to a value very close to that found for the complexes $[Fe(\eta\text{-}CH_2{=}CHX)(CO)_4]$; this in indeed found for the more electron-accepting substituents such as Br and I[3] (Table 2).

Another interesting aspect is the effect of substituent X on the rate constant k. Figure 2 shows the variation in $-\log k$ with the pK_b values for the anilines[13] from which the Schiff bases are obtained. The plot is linear, apart from the point for NMe_2 (which may be due to

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[11] G. Cardaci and V. Narciso, *J.C.S. Dalton*, 1972, 2289; G. Cardaci, *Internat. J. Chem. Kinetics*, 1973, **5**, 805; *J. Organometallic Chem.*, 1974, **76**, 385.

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[13] D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965.

specific interaction), and decreases with increasing pK_b. This indicates that electron-attracting substituents decrease the rate constant of the dissociation reactions of the complexes [Fe(CO)$_4$L]. Since the product of dissociation is always [Fe(CO)$_4$], whatever the initial complex, and since the energy of the activated complex is not strongly influenced by the substituent,[11] this behaviour parallels the thermodynamic stability of the complexes [Fe(CO)$_4$L].

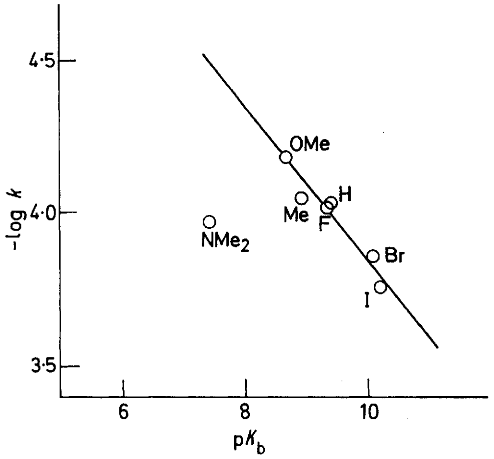

FIGURE 2 Plot of $-\log k$ against pK_b (of the anilines from which the Schiff bases were obtained) for reaction (3)

The above behaviour is different from that of the complexes [Fe(η-CH$_2$=CHX)(CO)$_4$], which are stabilised by electron-attracting substituents. For these complexes the substituent effect may also be extended to good electron-attracting substituents such as OH. The complex [Fe(η-CH$_2$=CHOH)(CO)$_4$] has recently been prepared:[14] it reacts rapidly with phosphinic ligands and decomposes even at —70 °C. If, as for the olefinic complexes, the mechanism of decomposition proceeds *via* dissociation of the Fe–CH$_2$=CHOH bond, the greater reactivity indicates a lower stability, in agreement with the substituent effect in η-olefin complexes.

A σ bond between the ligand and the iron atom, and a π bond from the iron to the organic ligand, contribute to the strength of the iron–ligand bond. Electron-attracting substituents strengthen the π bond and weaken the σ bond. The observed effects of substituents in the olefinic complexes lead to the conclusion that it is the π bond which determines the stability of these complexes. This is opposite to the situation in the Schiff bases considered here where the σ bond is mainly responsible for the stability.

As the two types of complex also differ in stereochemistry, the η-olefin complexes having the olefinic substituent in the plane of the trigonal bipyramid[15] whilst the Schiff base is apical,[16] it may be concluded that substituents in apical positions are mainly stabilised by the σ bond while those in equatorial positions are stabilised by the π bond. This is in agreement with some theoretical conclusions on the relative contributions of π and σ bonding in trigonal-bipyramidal five-coordinate d^8 complexes.[17]

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