Journal of Organometallic Chemistry, 90 (1974) 49—52

THE MECHANISM OF SUBSTITUTION OF π-(PhCH=CHCOR)Fe(CO)$_3$ COMPLEXES WITH PPh$_3$, AsPh$_3$ AND SbPh$_3$

G. CARDACI and G. CONCETTI

Institute of Physical Chemistry, University of Perugia, Perugia (Italy)

(Received November 11th, 1974)

Summary

The reaction between π-(PhCH=CHCOR)Fe(CO)$_3$ (R = H, CH$_3$, Ph) and L (L = PPh$_3$, AsPh$_3$, SbPh$_3$) in acetone occurs in two steps. The products of the first step are the π-(PhCH=CHCOR)Fe(CO)$_3$L complexes, which in the second step yield Fe(CO)$_3$L$_2$ and π-(PhCH=CHCOR)Fe(CO)$_2$L. The kinetic results indicate that the first step is association of the substrate with the ligand. The variation of the ratio [Fe(CO)$_3$L$_2$]/[π-(PhCH=CHCOR)Fe(CO)$_2$L] with L suggests three different reaction paths for the second step.

Introduction

Reactions between Group V ligands and organometallic carbonyl complexes have been studied extensively and substitution of the hydrocarbon [1] or of the CO [2] group has been observed. This behaviour was also observed for the π-dieneiron tricarbonyl [3] and π-heterodieneiron tricarbonyl [4, 5] complexes.

In this work we have studied the behaviour of π-(PhCH=CHCOR)Fe(CO)$_3$ complexes in an attempt to detect the formation of intermediate olefinic π-(PhCH=CHCOR)Fe(CO)$_3$L complexes.

During completion of this work, other authors [6] reported the formation of π-(RCH=CHCOR')Fe(CO)$_3$L complexes with very basic phosphinic ligands.

Experimental

The complexes π-(PhCH=CHCOR)Fe(CO)$_3$ (R = H, CH$_3$, Ph) were prepared as described elsewhere [5,7].

The complexes π-(PhCH=CHCOR)Fe(CO)$_2$L (L = PPh$_3$, AsPh$_3$, SbPh$_3$) were freed from the disubstituted Fe(CO)$_3$L$_2$ complexes by chromatography on Al$_2$O$_3$ using hexane as supporting liquid, and a 1/3 mixture of CH$_2$Cl$_2$/hexane as eluent.

TABLE 1

IR STRETCHING FREQUENCIES FOR π-(PhCH=CHCOR)$Fe(CO)_3L$ AND π-(PhCH=CHCOR)$Fe(CO)_2L$ COMPLEXES IN HEXANE

		$\nu(CO)$ (cm^{-1})	
R	L	π-(PhCH=CHCOR)$Fe(CO)_3L$	π-(PhCH=CHCOR)$Fe(CO)_2L$
H	PPh_3	2047, 1980, 1962	2000, 1947
H	$AsPh_3$	2050, 2057, 1982, 1965	2000, 1951
H	$SbPh_3$	2034, 1972, 1960	1994, 1947
CH_3	PPh_3	2040, 1977, 1962	2002, 1947
CH_3	$AsPh_3$	2052, 1982, 1962	2002, 1942
CH_3	$SbPh_3$	2044, 1972, 1962	1997, 1945
Ph	PPh_3	2047, 1991, 1962	2000, 1947
Ph	$AsPh_3$	2050, 1982, 1964	2002, 1947
Ph	$SbPh_3$	2027, 1992, 1964	2000, 1947

The complexes π-(PhCH=CHCOR)$Fe(CO)_3L$ were not separated but were identified by their IR CO stretching bands (Table 1). The structure of these complexes is probably trigonal bipyramidal, as observed for other Fe^0 complexes [8]. The three stretching bands of the CO group suggest that neither PPh_3 nor PhCH=CHCOR ligands are simultaneously apical in the bipyramid, but probably PPh_3 is in the apical and PhCH=CHCOR is in the equatorial position.

The kinetic runs were performed using a ten-fold excess of PPh_3 in carefully deaerated acetone. The pseudo-first-order rate constants were measured by following the disappearance of the CO stretching band at the higher frequency of the reacting complex and the appearance of the CO stretching frequency due to $Fe(CO)_3(PPh_3)_2$; at $[PPh_3] < 10^{-1}$ M, these rate constants are equal within the limits of experimental error, at $[PPh_3] > 10^{-1}$ M the rate constants differ and the formation of the intermediate π-(PhCH=CHCOR)-$Fe(CO)_3L$ is observed.

Spectrophotometric measurements were carried out in NaCl cells on a Perkin—Elmer 257 instrument. The temperature of reaction was 40°.

Results and discussion

The stoichiometry of the reaction is as follows:

$$\pi\text{-(PhCH=CHCOR)Fe(CO)}_3 + (1+\alpha)\,\text{L} \rightarrow \alpha\,\text{Fe(CO)}_3\text{L}_2 +$$
$$(1-\alpha)\,\pi\text{-(PhCH=CHCOR)Fe(CO)}_2\text{L} + (1-\alpha)\,\text{CO} + \alpha\,\text{(PhCH=CHCOR)} \qquad (1)$$

α is the fraction of $Fe(CO)_3L_2$ per mole of the reacting complex.

The reaction occurs in two steps. In the first, π-(PhCH=CHCOR)$Fe(CO)_3L$ complexes are formed and the kinetic results (Table 2) show that this step is of second-order and the mechanism is associative with the ligand PPh_3.

The intermediate π-(PhCH=CHCOR)$Fe(CO)_3L$ complexes react further to yield $Fe(CO)_3L_2$ and π-(PhCH=CHCOR)$Fe(CO)_2L$ complexes in the ratio

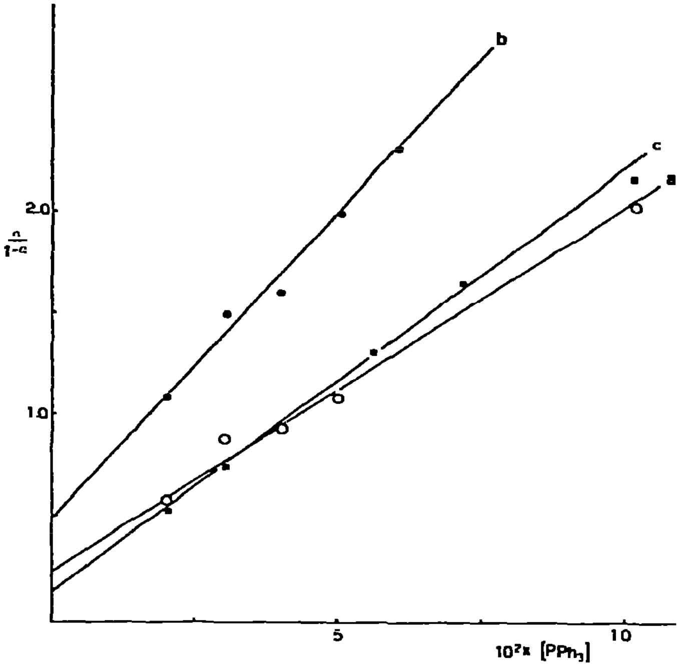


Fig. 1. Plot of $\alpha/(1-\alpha)$ vs. PPh$_3$ for reaction 1 in acetone at 40° with R = H (a), CH$_3$ (b), Ph (c).

$\alpha/1-\alpha$. This ratio increases with the concentration and the basicity of the ligand L. Figure 1 shows the plot of the $\alpha/1-\alpha$ versus the concentration of PPh$_3$; this plot is linear and the intercept is non-zero.

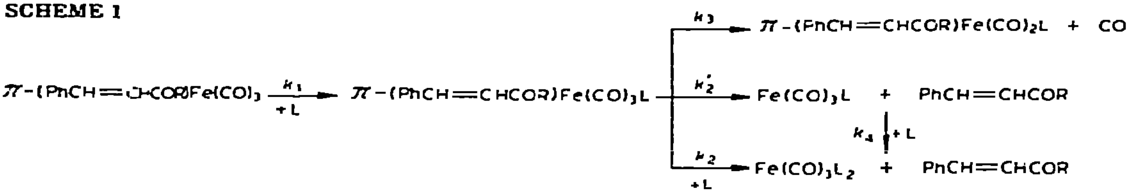
These experimental results may be explained on the basis of Scheme 1.

TABLE 2

THE RATIO $\alpha/(1-\alpha)$ AND SECOND-ORDER RATE CONSTANTS FOR REACTION 1 IN ACETONE AT 40°

π-(PhCH=CHCOR)Fe(CO)$_3$ R	10^2[PPh$_3$] (M)	$10^3 k_1$ (M^{-1} sec^{-1})	$\alpha/(1-\alpha)$	k_2/k_3 (M^{-1})	k'_2/k_3	k_2/k'_2 (M^{-1})
H	2.12		0.57	17.7	0.240	74
H	3.01		0.88			
H	4.01		0.94			
H	5.01	4.70	1.07			
H	10.20	4.60	2.04			
CH$_3$	2.00		1.07	32.0	0.490	65
CH$_3$	3.10		1.50			
CH$_3$	4.05		1.61			
CH$_3$	5.10	7.43	2.00			
CH$_3$	6.03		2.33			
CH$_3$	10.30	7.30				
Ph	2.00		0.56	20.4	0.150	136
Ph	3.02		0.77			
Ph	5.10	4.71				
Ph	5.60		1.32			
Ph	7.14		1.65			
Ph	10.10	4.55	2.16			

SCHEME 1



If k_4 [L] ≫ k'_2, as is reasonable, the ratio $\alpha/(1-\alpha)$ is given by eqn. 2. This accounts for the linear trend in Fig. 1.

$$\frac{\alpha}{1-\alpha} = \frac{k_2}{k_3}[\mathrm{L}] + \frac{k'_2}{k_3} \qquad (2)$$

On the basis of expression 2 the values k_2/k_3, k'_2/k_3 and k_2/k'_2 are obtained and are given in Table 2.

Equation 2 shows that $Fe(CO)_3L_2$ is formed by two parallel pathways, one associative with L and the other dissociative. This mechanism is different from that observed with square planar olefinic complexes [9] which react by an associative mechanism and with octahedral olefinic complexes [10], which react by a dissociative mechanism.

The ratio k_2/k'_2 gives the rate of the associative relative to that of the dissociative path for the formation of $Fe(CO)_3L_2$; the ratio values decrease in the order Ph > H > CH_3, thus, the CH_3 substituent favours the dissociative path, in accord with substituent effects found in the olefinic complexes studied previously [11].

At this stage of the investigation it is impossible to say whether or not the formation of the π-(PhCH=CHCOR)$Fe(CO)_2L$ complexes proceeds via an intramolecular chelation mechanism, particularly in view of the results obtained for the formation of π-(PhCH=CHCOR)$Fe(CO)_3$ from π-(PhCH=CHCOR)$Fe(CO)_4$ [12].

References

1 F. Zingales, A. Chiesa and F. Basolo, J. Amer. Chem. Soc., 88 (1966) 2707; A. Pidcock and B.W. Taylor, J. Chem. Soc. A, (1967) 877.
2 T.A. Manuel and F.G.A. Stone, J. Amer. Chem. Soc., 82 (1960) 366.
3 A. Reckziegel and M. Bigorgne, J. Organometal. Chem., 3 (1965) 341.
4 S. Otsuka, T. Yoshida and A. Nakamura, Inorg. Chem., 6 (1967) 20.
5 A.M. Brodie, B.F.G. Johnson, P.L. Josty and J. Lewis, J. Chem. Soc. Dalton, (1972) 2031.
6 A. Vessieres and A. Dixneuf, Tetrahedron Lett., (1974) 1499.
7 E. Koerner Von Gustorf, F.W. Grevels, C. Krüger, G. Olbrich, F. Mark, D. Shulz and R. Wagner, Z. Naturforsch. B, 27 (1972) 392.
8 A.R. Luxmoore and M.R. Truter, Acta Crystallogr., 15 (1962) 1117;
C. Pedone and A. Sirigu, Inorg. Chem., 7 (1968) 2614.
9 C.E. Holloway and J. Fogelman, Can. J. Chem., 48 (1970) 3802.
10 M. Wrighton, G.S. Hammond and H.B. Gray, J. Amer. Chem. Soc., 93 (1971) 6048.
11 G. Cardaci and V. Narciso, J. Chem. Soc. Dalton, (1972) 2289;
G. Cardaci, Int. J. Chem. Kinet., 5 (1973) 805.
12 G. Cardaci, J. Amer. Chem. Soc., in press.