

THE MECHANISM OF SUBSTITUTION OF π -(PhCH=CHCOR)Fe(CO)₃ COMPLEXES WITH PPh₃, AsPh₃ AND SbPh₃

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Summary

The reaction between π -(PhCH=CHCOR)Fe(CO)₃ (R = H, CH₃, Ph) and L (L = PPh₃, AsPh₃, SbPh₃) in acetone occurs in two steps. The products of the first step are the π -(PhCH=CHCOR)Fe(CO)₃L complexes, which in the second step yield Fe(CO)₃L₂ and π -(PhCH=CHCOR)Fe(CO)₂L. The kinetic results indicate that the first step is association of the substrate with the ligand. The variation of the ratio [Fe(CO)₃L₂] / [π -(PhCH=CHCOR)Fe(CO)₂L] 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)₃L complexes.

During completion of this work, other authors [6] reported the formation of π -(RCH=CHCOR')Fe(CO)₃L complexes with very basic phosphinic ligands.

Experimental

The complexes π -(PhCH=CHCOR)Fe(CO)₃ (R = H, CH₃, Ph) were prepared as described elsewhere [5,7].

The complexes π -(PhCH=CHCOR)Fe(CO)₂L (L = PPh₃, AsPh₃, SbPh₃) were freed from the disubstituted Fe(CO)₃L₂ complexes by chromatography on Al₂O₃ using hexane as supporting liquid, and a 1/3 mixture of CH₂Cl₂/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

R	L	$\nu(\text{CO}) (\text{cm}^{-1})$	
		π -(PhCH=CHCOR)Fe(CO) ₃ L	π -(PhCH=CHCOR)Fe(CO) ₂ L
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

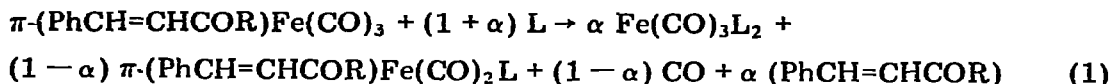
The complexes π -(PhCH=CHCOR)Fe(CO)₃L were not separated but were identified by their IR CO stretching bands (Table 1). The structure of these complexes is probably trigonal bipyramidal, as observed for other Fe⁰ complexes [8]. The three stretching bands of the CO group suggest that neither PPh₃ nor PhCH=CHCOR ligands are simultaneously apical in the bipyramid, but probably PPh₃ is in the apical and PhCH=CHCOR is in the equatorial position.

The kinetic runs were performed using a ten-fold excess of PPh₃ 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(PPh₃)₂; at [PPh₃] < 10⁻¹ M, these rate constants are equal within the limits of experimental error, at [PPh₃] > 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:



α is the fraction of Fe(CO)₃L₂ 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 PPh₃.

The intermediate π -(PhCH=CHCOR)Fe(CO)₃L complexes react further to yield Fe(CO)₃L₂ and π -(PhCH=CHCOR)Fe(CO)₂L complexes in the ratio

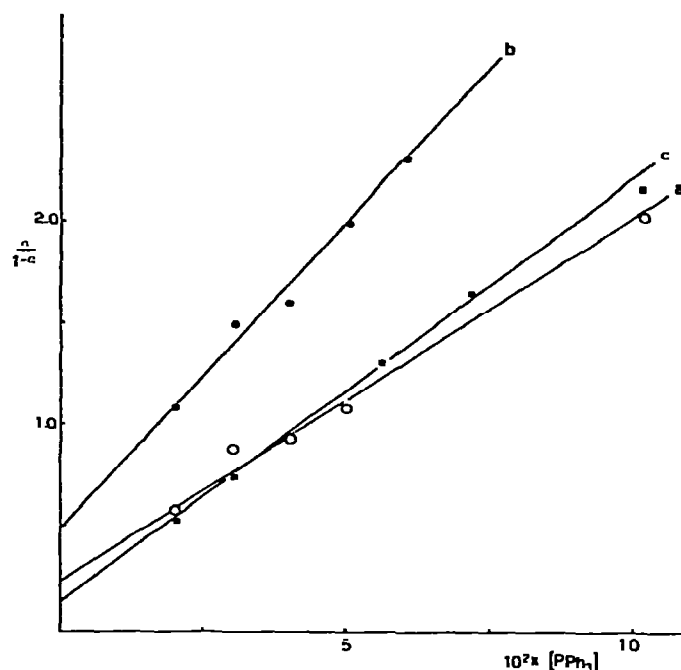


Fig. 1. Plot of $\alpha/(1 - \alpha)$ vs. PPh_3 for reaction 1 in acetone at 40° with $\text{R} = \text{H}$ (a), CH_3 (b), Ph (c).

$\alpha/1 - \alpha$. 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°

$\pi\text{-(PhCH=CHCOR)Fe(CO)}_3$	$10^2 [\text{PPh}_3]$	$10^3 k_1$	$\alpha/(1 - \alpha)$	k_2/k_3	k'_2/k_3	k_2/k'_2
R	(M)	($\text{M}^{-1} \text{sec}^{-1}$)		(M^{-1})		(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	5.50		1.32			
Ph	7.14		1.65			
Ph	10.10	4.55	2.16			

