Contribution from the Department of Chemistry,
The University of York, Heslington, York YO1 5DD, United Kingdom

Substitution Reactions of Indenyl and Tetrahydroindenyl Iron Carbonyl Complexes: A Kinetic Study

D. J. Jones and R. J. Mawby

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Carbonyl substitution reactions of the indenyl complex π–$C_9H_7Fe(CO)_2I$ proceed by an S_N1 mechanism, and are faster than the analogous reactions of the cyclopentadienyl complex π–$C_5H_5Fe(CO)_2I$ by a factor of ca. 600 at 95° C. This acceleration cannot be attributed to the greater crowding around the iron atom in the indenyl complex since the even more crowded tetrahydroindenyl complex π–$C_9H_{11}Fe(CO)_2I$ reacts at a similar rate to the cyclopentadienyl complex. It is suggested that the acceleration may be due to a lowering in energy of the activated state caused by an interaction between the aromatic six-membered ring and the metal atom, which partly compensates for the loss of bonding to the leaving CO group.

Introduction

Studies of carbonyl substitution reactions of the cyclopentadienyl complexes π–$C_5H_5Mo(CO)_3X$ ($X = Cl, Br, I$) and complexes π–$C_9H_7Mo(CO)_3X$ in which the cyclopentadienyl ligand has been replaced by an indenyl ligand indicate that this change in ligand causes a large change in the rates of the substitution reactions. Thus, the values for the rate constants for reactions:

$$\pi\text{–}ZMo(CO)_3X + L \rightarrow \pi\text{–}ZMo(CO)_2LX + CO \qquad (1)$$

at 10° C are several thousand times larger for the indenyl complexes[1] ($Z = C_9H_7$) than for the cyclopentadienyl complexes[2] ($Z = C_5H_5$).

Several factors, however, complicate the study of these reactions. One is the tendency of the cyclopentadienyl complexes with $X = Br$ and I to react in a manner suggestive of a radical mechanism, an induction period of variable length being followed by a reaction whose rate is not reproducible from one run to another. The second complicating factor is the presence of competing S_N1 and S_N2 pathways for many of the reactions, and the third is the tendency of some nucleophiles L to attack the cyclopentadienyl or indenyl ligand rather than replace a carbonyl ligand.[1,2]

For this reason, we have extended our studies to some analogous iron complexes, and this paper deals with the rate and mechanism of substitution reactions of the cyclopentadienyl complex π–$C_5H_5Fe(CO)_2I$, the indenyl complex π–$C_9H_7Fe(CO)_2I$ and the tetrahydroindenyl complex (in which the aromatic character of the *six-membered* ring has been destroyed) π–$C_9H_{11}Fe(CO)_2I$.

Experimental Section

All preparative and kinetic work was carried out under an atmosphere of pure dry nitrogen, except where stated otherwise. Solvents were dried by standard procedures, and both solvents and ligands used for kinetic studies were distilled under nitrogen shortly before use. Rate constants were obtained by monitoring the disappearance of the band due to the higher energy C–O stretching mode in the complexes π–$ZFe(CO)_2I$. Rates were reproducible to ± 3% at worst. In all cases where the C–O stretching band of the product π–$ZFe(Co)P(OR)_3I$ did not overlap with bands due to π–$ZFe(CO)_2I$, rates of appearance of π–$ZFe(CO)P(OR)_3I$ were also calculated and found to be in good agreement with rates of disappearance of π–$ZFe(CO)_2I$. All bands used obeyed Beer's law over the appropriate concentration range. Details of the techniques for treating the kinetic data have been described in an earlier paper.[3]

Preparation of Complexes. $[\pi$–$C_5H_5Fe(CO)_2]_2$. This was prepared by the method of King and Stone.[4]

$[\pi$–$C_9H_7Fe(CO)_2]_2$. A mixture of $Fe(CO)_5$ (2 g), indene (1 g) and petroleum ether (100–120° C, 25 ml) was heated under reflux under an atmosphere of CO for 16hr. After the solution had cooled to room temperature, the crude product was removed by filtration and purified by chromatography on silica gel. Elution with benzene followed by slow evaporation of the benzene solution yielded the pure product.

$[\pi$–$C_9H_{11}Fe(CO)_2]_2$. Each of the two methods described in the literature[5] was tried. Catalytic reduction of $[\pi$–$C_9H_7Fe(CO)_2]_2$ was found to be the more successful route, giving virtually quantitative yields after 72 hr under 1 atmosphere of H_2.

π–$ZFe(CO)_2I$. These complexes ($Z = C_5H_5$, C_9H_7, C_9H_{11}) were prepared by dropwise addition of a dilute solution of I_2 in CH_2Cl_2 to a stirred solution of $[\pi$–$ZFe(CO)_2]_2$ in CH_2Cl_2. The progress of the reaction was monitored by infra-red spectroscopy in the

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(1) A.J. Hart-Davis, C. White and R.J. Mawby, *Inorg. Chim. Acta*, *4*, 441 (1970).
(2) C. White and R.J. Mawby, *Inorg. Chim. Acta*, *4*, 261 (1970).
(3) A.J. Hart-Davis and R.J. Mawby, *J. Chem. Soc.* (A), 2403 (1969).
(4) R.B. King and F.G.A. Stone, *Inorg. Synth.*, *7*, 99 (1963).
(5) B.F. Hallam and P.L. Pauson, *J. Chem. Soc.*, 646 (1958).

Table I. Analytical Data

	M. Pt.[a] °C	Found %C	Found %H	Found %Fe	Calculated %C	Calculated %H	Calculated %Fe
$[\pi\text{—}C_9H_7Fe(CO)_2]_2$	196-7 [b]	58.1	3.3	24.6	58.1	3.1	24.7
$\pi\text{—}C_9H_7Fe(CO)_2I$	128	37.6	2.2	15.8	37.3	2.0	15.8
$\pi\text{—}C_9H_7Fe(CO)P(OPh)_3I$	125	54.1	3.7	8.5	53.0	3.5	8.8
$[\pi\text{—}C_9H_{11}Fe(CO)_2]_2$	147-8 [c]	56.8	4.7	24.2	57.1	4.8	24.2
$\pi\text{—}C_9H_{11}Fe(CO)_2I$	80	36.6	3.1	16.5	36.9	3.1	15.6
$\pi\text{—}C_9H_{11}Fe(CO)P(OPh)_3I$	110	51.4	4.3	8.7	52.5	4.1	8.7

[a] With decomposition. [b] Literature[5] M.Pt. 198°C. [c] Literature[5] M.Pt. 148°C

Table II. Infra-red Spectra in the C—O stretching Region in *n*-octane solution.

	cm^{-1}
$\pi\text{—}C_5H_5Fe(CO)_2I$	2043, 2004
$\pi\text{—}C_9H_7Fe(CO)_2I$	2038, 1997
$\pi\text{—}C_9H_{11}Fe(CO)_2I$	2037, 1995
$\pi\text{—}C_5H_5Fe(CO)P(OEt)_3I$	1965
$\pi\text{—}C_9H_7Fe(CO)P(OEt)_3I$	1968
$\pi\text{—}C_9H_{11}Fe(CO)P(OEt)_3I$	1954
$\pi\text{—}C_5H_5Fe(CO)P(OPh)_3I$	1988
$\pi\text{—}C_9H_7Fe(CO)P(OPh)_3I$	1970
$\pi\text{—}C_9H_{11}Fe(CO)P(OPh)_3I$	1978

Table III. Observed Rate Constants for Reactions of $\pi\text{—}C_5H_5Fe(CO)_2I$ in *n*-octane.

Ligand	Temp. (°C)	Ligand Concentration (*M*)	10^4 k_{obs} (sec^{-1})
$P(OEt)_3$	96.2	0.360	4.26
	102.0	0.360	8.00
	107.0	0.220	14.1
		0.360	14.3
	110.0	0.220	19.2
		0.350	19.4
		0.400	19.4
$P(OPh)_3$	89.3	0.200	1.47
	95.2	0.210	3.10
	100.4	0.199	5.76
	102.0	0.124	6.76
		0.218	6.64
		0.292	6.53
	107.0	0.140	11.2
		0.400	10.6

C–O stretching region, and addition of iodine was stopped when bands due to $[\pi\text{–}ZFe(CO)_2]_2$ had disappeared. After removal of solvent, the residue was purified by chromatography on silica gel. Excess iodine was removed by elution with petroleum ether, and $\pi\text{–}ZFe(CO)_2I$ by elution with CH_2Cl_2. Slow evaporation of the CH_2Cl_2 solutions yielded pure products. $\pi\text{–}ZFe(CO)P(OPh)_3I$. These complexes ($Z = C_9H_7$, C_9H_{11}) were prepared by heating $\pi\text{–}ZFe(CO)_2I$ (0.5 g) with excess $P(OPh)_3$ in *n*-octane (100 ml) at 100° C until the infra-red spectrum of the reaction mixtures indicated complete conversion to $\pi\text{–}ZFe(CO)P(OPh)_3I$. On allowing the solutions to cool to room temperature, crystals of the products were obtained in a pure state.

The cyclopentadienyl complexes have been characterized by Brown *et al.*[6] Analytical data for indenyl and tetrahydroindenyl complexes are given in Table I.

Equipment. The infra-red spectra in Table II were recorded on a Unicam SP200G spectrophotometer. Kinetic studies were performed on a Perkin-Elmer 257 spectrophotometer.

Results

The complexes $\pi\text{–}C_5H_5Fe(CO)_2I$, $\pi\text{–}C_9H_7Fe(CO)_2I$ and $\pi\text{–}C_9H_{11}Fe(CO_2I$ all react quantitatively with ligands $P(OR)_3$ ($R = Et$, Ph) both in *n*—octane and in di—*n*—butyl ether according to equation (2):

$$\pi\text{–}ZFe(CO)_2I + P(OR)_3 \rightarrow \pi\text{–}ZFe(CO)P(OR)_3I + CO \qquad (2)$$

The reactions are all first order in iron complex. The product with $Z = C_5H_5$ and $R = Ph$ has been characterized by Brown *et al.*,[6] and we have characterized the analogous complexes with $Z = C_9H_7$ and C_9H_{11}. (In other solvents such as chloroform or benzene, mixtures of products, of which one component may be the ionic species $[\pi\text{–}ZFe(CO)_2P(OR)_3]I$, are formed).

Rate constants for the reactions of $\pi\text{–}C_5H_5Fe(CO)_2I$ in *n*—octane and di—*n*—butyl ether over temperature ranges of slightly under 10° have been reported by Brown *et al.*,[6] and used to calculate activation parameters. In order to obtain more accurate parameters, we have used a wider temperature range. The values obtained in *n*—octane are given in Table III. The rate of reaction of $\pi\text{–}C_5H_5Fe(CO)_2I$ with $P(OEt)_3$ is independent of the ligand concentration, but for the reaction with $P(OPh)_3$ there is a slight decrease in rate with increasing ligand concentration. The effect is small, and is probably attributable to a change in the nature of the solvent with increasing $P(OPh)_3$ concentration. No immediate change in visible/ultra-violet or infra-red spectra of the complexes $\pi\text{–}ZFe(CO)_2I$ in *n*-octane solution occurs on addition of $P(OPh)_3$, which makes any more specific «molecule pairing» interaction between complex and ligand prior to reaction (2) unlikely. We conclude that the S_N1 mechanism previously proposed[6] for these reactions, in which the rate-determining step is the loss of a carbonyl group, is correct.

$$\pi\text{–}ZFe(CO)_2I \xrightarrow[-CO]{\text{slow}} \pi\text{–}ZFe(CO)I \xrightarrow[+P(OR)_3]{\text{fast}} \pi\text{–}ZFe(CO)P(OR)_3I$$

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(6) D.A. Brown, H.J. Lyons, A.R. Manning and J.M. Rowley, *Inorg. Chim. Acta*, 3, 346 (1969).

Table IV. Observed Rate Constants for Reactions of π—$C_9H_7Fe(CO)_2I$

Solvent	Ligand	Temp. (°C)	Ligand Concentration (*M*)	10^4 k_{obs} (sec^{-1})
n-octane	$P(OEt)_3$	44.8	0.285	2.31
		50.0	0.299	4.55
		55.8	0.240	13.2
		60.0	0.223	18.9
			0.560	19.2
	$P(OPh)_3$	40.0	0.114	0.88
			0.329	0.79
		44.8	0.179	1.86
			0.553	1.48
		50.0	0.261	3.67
			0.412	3.25
		55.3	0.213	7.59
		55.8	0.312	8.02
			0.421	7.46
		60.0	0.200	15.9
			0.319	14.6
			0.445	13.2
di-*n*-butyl ether	$P(OEt)_3$	50.1	0.316	3.54
		55.0	0.292	6.64
			0.363	6.67
		60.0	0.290	12.5
		65.3	0.288	25.7
	$P(OPh)_3$	45.0	0.193	1.27
		49.7	0.181	2.64
		55.0	0.210	4.81
			0.255	5.03
			0.329	4.99
		60.0	0.231	10.1

Table V. Observed Rate Constants for Reactions of π—$C_9H_{11}Fe(CO)_2I$ in *n*-octane.

Ligand	Temp. (°C)	Ligand Concentration (*M*)	10^4 k_{obs} (sec^{-1})
$P(OEt)_3$	96.2	0.340	2.04
	99.5	0.557	2.95
	107.0	0.210	6.70
		0.350	6.67
	110.0	0.240	8.92
		0.380	8.89
		0.560	8.94
$P(OPh)_3$	91.6	0.154	1.06
	95.2	0.223	1.55
	99.5	0.218	2.61
		0.330	2.50
		0.438	2.39
	100.4	0.198	2.76
	107.0	0.181	5.91
		0.220	5.87
		0.438	5.64
	109.0	0.124	7.39
		0.226	7.25
		0.277	7.20

Attempts to study the reactions of π—$C_5H_5Fe(CO)_2I$ in di—*n*—butyl ether yielded rate constants of poor reproducibility.

Activation parameters derived from the rate constants for the reaction with $P(OEt)_3$ in *n*—octane are given in Table V. These differ appreciably from those given by Brown *et al.*[6] ($\Delta H^* = 26.84$ kcal. mol.$^{-1}$; $\Delta S^* = -4.22$ e.u.), the value for the entropy of activation being *positive*, as expected for a reaction with a dissociative rate-determining step. We estimate that the parameters given in Table VI are correct to ± 1.0 kcal. mol^{-1} for ΔH^* and ± 2.5 e.u. for ΔS^*.

The reactions of the indenyl complex π—$C_9H_7Fe(CO)_2I$ with both $P(OEt)_3$ and $P(OPh)_3$ in di—*n*—butyl ether yield reproducible rate constants which are independent of ligand concentration (Table IV). In *n*—octane the rate of reaction with $P(OEt)_3$ is again independent of ligand concentration but – as in the case of π—$C_5H_5Fe(CO)_2I$ – there is a slight negative dependence on ligand concentration when $P(OPh)_3$ is used. Evidently the mechanism of carbonyl substitution reactions of π—$C_9H_7Fe(CO)_2I$ is the same as that for π—$C_5H_5Fe(Co)_2)I$. Activation data are given in Table VI for both ligands in di—*n*—butyl ether and for $P(OEt)_3$ in *n*—octane.

Similar behaviour was observed for the tetrahydroindenyl complex π—$C_9H_{11}Fe(CO)_2I$. Here reproducible rate constants could not be obtained in di—*n*—butyl ether, and data are given in Table V for reactions in *n*—octane only. Activation parameters for the reaction with $P(OEt)_3$ are given in Table VI.

Discussion

In order to compare reaction rates at a particular temperature, it is necessary to extrapolate the data for the reactions of the indenyl complex, π—$C_9H_7Fe(CO)_2I$, to the temperatures used for the other two complexes. Relative rates for the reactions of the three complexes with $P(OEt)_3$ in *n*—octane at 95.2° C are given below.

π—$C_5H_5Fe(CO)_2I$	π—$C_9H_7Fe(CO)_2I$	π—$C_9H_{11}Fe(CO)_2I$
1.0	575	0.5

Table VI. Activation Data for Reactions of Complexes π–ZFe $(CO)_2I$

Complex	Solvent	Ligand	ΔH* kcal. mol^{-1}	ΔS* e.u.
π–$C_5H_5Fe(CO)_2I$	*n*-octane	$P(OEt)_3$	30.4	7.9
π–$C_9H_7Fe(CO)_2I$	*n*-octane	$P(OEt)_3$	29.0	15.7
π–$C_9H_{11}Fe(CO)_2I$	*n*-octane	$P(OEt)_3$	29.4	3.8
π–$C_9H_7Fe(CO)_2I$	di-*n*-butyl ether	$P(OEt)_3$	28.3	13.0
π–$C_9H_7Fe(CO)_2I$	di-*n*-butyl ether	$P(OPh)_3$	27.9	11.1

The increase in rate when the cyclopentadienyl ligand is replaced by an indenyl group is clearly not due to greater crowding round the iron atom, since the tetrahydroindenyl complex (which if anything will be even more crowded than the indenyl complex) reacts at a rate which is even slower than that of the cyclopentadienyl complex.

There is no indication from the C–O stretching frequencies for the three molecules (see Table II) that the Fe–C–O bonding in the ground state of the indenyl complex differs from that for the other two complexes: indeed the spectra of the indenyl and tetrahydroindenyl complexes in this region are virtually identical. We conclude that the marked increase in rate for the indenyl complex is caused by a lowering in the energy of the activated state relative to the ground state. This might imply some degree of participation by the aromatic six-membered ring in the bonding in the activated state to compensate for the weakening of the bond to the leaving carbonyl group. This would be in marked contrast to the situation in the ground state of π–indenyl complexes, where there is no evidence for such an interaction (see, for example, the recent report[7] on the structure of π–$C_9H_7Mo(CO)_3I$, whose overall geometry is closely related to that of *cyclopentadienyl* complexes of molybdenum(II)).

Comparison of the activation parameters (Table VI) for the reactions of the three complexes shows that the increase in rate for the indenyl complex is reflected mainly in an increase in the *entropy* of activation, rather than a decrease in the activation enthalpy. This is the exact reverse of the situation for the analogous molybdenum complexes.[1] In view of the similar compositions of the two series of complexes, π–$ZFe(CO)_2X$ and π–$ZMo(CO_3X$, and the similar variations in the rate constant with variation in Z, this discovery is most surprising, and appears to cast considerable doubt on the meaningfulness of the breakdown of the free energy of activation into enthalpy and entropy contributions.

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(7) A. Mawby and G.E. Pringle, *J. Inorg. Nuclear Chem.*, in press.