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Solvent and Structural Effects in Substitution Reactions of Dicarbonyliodo(η-cyclohexa-1,3-dienyl) and Dicarbonyliodo(η-cyclo-hepta-1,3-dienyl)iron Complexes

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A comparison of the kinetics of substitution by phosphite ligands of dicarbonyliodo(η-cyclo-hexa-1,3-dienyl) and dicarbonyliodo(η-cyclo-hepta-1,3-dienyl)-iron complexes is reported. In all cases a dissociative mechanism is observed. The variation of rate with the size of the attached ring is in the sequence: Cyclohexadienyl > Cycloheptadienyl > Cyclopentadienyl which is not in accord with the observed carbonyl stretching frequencies. However, detailed solvent studies show that for the six and seven-membered ring compounds the transition state is more polar than the ground state which is the opposite of that observed for the cyclopentadienyl series. It is also suggested that solvents with comparable donor and acceptor qualities stabilize the dissociative transition state by a push–pull type mechanism.

Introduction

This paper is a continuation of our previous studies [1] of the carbonyl substitution reactions of a series of dicarbonyliodo(η-cyclopentadienyl) metals, $C_5H_5M(CO)_2X$, M = Fe, X = Cl, Br, I by various phosphite and phosphine ligands. It is well known that the majority of carbonyl substitution reactions of metal carbonyl complexes proceed via a dissociative mechanism [2] and for substitution of a series of related complexes *for which the transition state varies only slightly* a close correlation exists between reactivity and the structure of the ground state either in terms of theoretical quantities such as overlap populations, charge densities or experimental quantities such as ν(C–O) for the bond being substituted. In other cases, for example, *trans*-labilization where the transition state appears to vary considerably between different complexes, correlation between reactivity and ground state properties is poor [3].

It had been suggested that the presence of antibonding π ring orbitals in a cyclopentadienyl metal carbonyl complex promoted S_N2 nucleophilic attack but this was disproved by our previous studies [1, 4]. In the case of related metal carbonyl complexes of dienes of varying ring sizes with similar electronic structures it is necessary to establish the relative importance of electronic and steric effects and so the effect of ring size on the mechanism and rate of carbonyl substitution has been studied. Previous comparisons [5] between cyclopentadienyl complexes and the analogous indenyl systems showed a remarkable increase in rate of carbonyl substitution which was attributed to a reduction in activation energy caused by interaction between the six-membered ring and the metal atom. Similar results were reported for the closely related analogous tricarbonylhalogenocyclopentadienyl molybdenum and analogous indenyl systems [6] although in these cases an S_N2 associative pathway is also observed. However, some of these reactions may be complicated by additional factors such as a) free-radical mechanisms, b) direct attack by a nucleophile on the complexed ring, c) instability of complexes in certain solvents and d) formation of more than one product; so caution is required. Reaction of PPh_3 with a series of tricarbonyl ring iron complexes where the ring was varied in the sequence: η-cyclohexa-1,3-diene; η-cyclohepta-1,3,5-triene; η-cycloocta-1,3-diene showed that the largest cyclic diene is the most readily displaced [7]. Carbonyl substitution was only observed for the six-membred ring complex which showed a large activation energy and there was no obvious correlation between carbonyl substitution and size of the attached ring.

Experimental

Solvent Purification

Acetonitrile was purified as described by Cortere *et al.* [8]. (Method D and E).

Benzene and xylene were distilled over sodium and then passed over a short alumina column and finally distilled over CaH_2 under N_2 atmosphere just before use.

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Di-n-Butyl ether was refluxed over HCl for 6–8 hours and distilled. It was further purified as described earlier [1].

Chloroform was first shaken with silica gel for 4 hours and re-distilled. Next it was passed over an alumina column and distilled, finally refluxed over calcium chloride for several hours and distilled out of contact of light just before use.

Nitrobenzene was dried over anhydrous $CaCl_2$ and passed over a short alumina column. It was re-distilled just before use.

Ligand Purification

The ligand triphenylphosphite was distilled under reduced pressure just before use.

Preparative Reactions

η-$ZFe(CO)_2I$ ($Z = C_6H_7$: C_7H_9 and C_9H_7) were prepared by literature methods [5, 9, 10]. η-$C_7H_9Fe(CO)P(OPh)_3I$ was prepared by refluxing η-$C_7H_9Fe(CO)_2I$ (0.8 gm) with a slight excess of triphenylphosphite in 50 ml of benzene for one and half hours. The mixture was filtered hot, and the solvent removed under reduced pressure to yield an oil. Addition of a drop of methanol caused the oil to break up and it was then recrystallized from chloroform–ligroin (60–80); 90% yield of the covalent monosubstituted product was obtained. There was no indication of an ionic product being formed. Analytical and infrared data are given in Table I. Infrared frequencies are accurate to ±1 cm^{-1}.

Reaction of η-$C_7H_9Fe(CO)_2I$ with PPh_3 gave two products: a normal covalent monosubstituted compound and an unidentified product with no CO stretching vibrations in the IR. Reactions were carried out in all solvents used for kinetics and satisfactory Beer's law plots obtained in them.

Kinetic Studies

Kinetic studies were carried out as described previously [1]. All solvents were re-distilled under nitrogen just before use. It was found that commercially obtained oxygen-free nitrogen caused a slight decomposition in the reaction, so it was further purified by passing through Fieser's solution (Pb acetate, silica gel and conc. H_2SO_4) just before it entered the presaturator at a constant flow rate. The importance of efficient removal of carbon monoxide during a substitution reaction has already been stressed. The observed rate constants were found to be independent of the rate of flow of nitrogen. It was also found that the ligand was the stabilising factor so η-$ZFe(CO)_2I$ was added to the thermostated solution of the ligand at zero time. Reaction was monitored by following the rate of disappearance of the high frequency carbonyl band of η-$ZFe(CO)_2I$ using a Perkin Elmer 457 or 337 infrared spectrophotometer. Comparison of the IR spectrum of a run after several half-lives with that of the product obtained in the above preparative experiments confirmed that all kinetic runs went to completion to the covalent product only. Good least square plots for first order kinetics were obtained in spite of lesser reproducibility in acetonitrile and nitrobenzene.

Rate constants were reproducible to 3% at the worst, however the reproducibility in acetonitrile and nitrobenzene was up to 7%. All reactions were carried out under pseudo-first order conditions with at least a tenfold excess of the ligand. Each reported rate constant is the mean of at least three runs. A number of concentrations of the ligand were used for each temperature, but only a summary of the rate data is given in Table II.

Results and Discussion

The values of the first-order rate constants, k 10^{-4} sec^{-1}, are given in Table II for a range of substrates and solvents. The corresponding activation parameters are given in Table III together with the known donor number (DN) and acceptor number (AN) of

TABLE I. Elemental Analysis and Infrared Carbonyl Stretching Frequencies ν(C–O) of the Series $ZFe(CO)_2I$, $ZFe(CO)P(OPh)_3I$ ($Z = \eta C_6H_7, \eta C_7H_9$) in n-Heptane.

Compound	% Found		% Calculated		ν(C–O) cm^{-1}
	C	H	C	H	
$\eta C_5H_5Fe(CO)_2I$	27.27	1.67	27.66	1.64	2043, 2004
$\eta C_6H_7Fe(CO)_2I$	29.97	2.51	30.1	2.51	2037, 2000
$\eta C_7H_9Fe(CO)_2I$	32.32	2.88	32.54	2.73	2035, 2000.4
$\eta C_9H_7Fe(CO)_2I$	36.94	1.96	37.3	2.0	2038, 1997.0
$\eta C_6H_7Fe(CO)P(OPh)_3I$	50.2	3.69	50.0	3.6	1987.8
$\eta C_7H_9Fe(CO)P(OPh)_3I$	50.82	3.90	50.6	4.04	1988.4
$\eta C_9H_7Fe(CO)P(OPh)_3I$	53.4	3.7	53.0	3.5	1971
$\eta C_7H_9Fe(CO)PPh_3I$	55.12	4.24	55.22	4.20	1954.4
$\eta C_7H_9Fe(CO)P(Ph)_2(C_2H_5)I$	50.04	4.72	50.23	4.56	1955.2
$\eta C_7H_9Fe(CO)P(OC_2H_5)_3I$	35.74	5.1	35.37	4.95	1984.0

TABLE II. Rates of Reaction of $ZFe(CO)_2I$ ($Z = \eta C_6H_7, \eta C_7H_9, \eta C_9H_7$) with $P(OPh)_3$ in Various Solvents.

Substrate	Solvent	Temp.	Ligand 10^2 Mol Litre^{-1}	10^4 k (sec^{-1})
$C_6H_7Fe(CO)_2I$	Xylene	53.00	5.07	5.45
			10.18	5.52
			15.20	5.51
			17.75	5.60
		56.30	5.08	7.96
		57.45	5.08	9.99
		59.85	5.08	12.69
		62.05	5.08	18.40
$C_6H_7Fe(CO)_2I$	Acetonitrile	43.65	5.08	4.35
			7.63	4.62
			10.17	4.68
		47.50	5.08	5.50
		50.60	5.08	6.75
		56.70	5.08	15.80
$C_6H_7Fe(CO)_2I$	Chloroform	47.35	5.08	3.36
			10.17	3.71
			15.20	3.74
		50.60	5.08	5.68
		53.90	5.08	8.40
		57.15	5.08	13.60
$C_7H_9Fe(CO)_2I$	Xylene	56.00	5.08	2.75
			10.17	2.61
			12.70	2.82
		62.00	5.08	5.52
		65.00	5.08	8.66
		68.00	5.08	12.47
$C_7H_9Fe(CO)_2I$	Benzene	59.97	5.08	4.59
			10.17	4.62
			15.70	4.64
		63.27	5.08	7.28
		65.40	5.08	8.60
		68.48	5.08	12.50
		70.05	5.08	15.60
$C_7H_9Fe(CO)_2I$	Di-n-butylether	56.00	2.50	3.42
			10.17	3.49
			15.20	3.54
		60.16	5.08	6.12
		62.67	5.08	8.60
		64.78	5.08	11.60
		66.78	5.08	14.60
	Chloroform	45.05	2.52	0.93
			5.08	0.92
			10.17	0.92
		49.75	5.08	1.81
		53.00	5.08	2.64
		55.55	5.08	3.48
		58.75	5.08	4.89
$C_7H_9Fe(CO)_2I$	Nitrobenzene	60.75	40.60	5.34
			81.20	5.52
			121.16	5.48
		63.80	40.60	6.93
		65.80	40.60	9.13
		69.30	40.60	12.43
		72.45	40.16	16.50

TABLE II. (Continued)

$C_7H_9Fe(CO)_2I$	Acetonitrile	50.92	5.08	5.94
			10.8	5.98
			12.17	5.91
		53.42	5.08	8.00
		56.67	5.08	11.00
		59.93	2.50	16.00
$C_9H_7Fe(CO)_2I$	Xylene	52.95	2.52	2.53
			5.08	2.58
			10.17	2.61
			15.20	2.64
		55.75	5.08	4.10
		58.27	5.08	6.05
		60.15	5.08	7.60
		62.85	5.08	10.65

TABLE III. Activation Parameters.

Substrate	Solvent	A.N.	D.N.	ΔS	E_a	10^4 k(sec^{-1}) at 56 °C
$C_5H_5Fe(CO)_2I$	Xylene	(~8.3)	(~0.1)	11.6	34.6	
	Nitrobenzene	14.8	4.4	10.5	33.5	
$C_6H_7Fe(CO)_2I$	Xylene	(~8.2)	(~0.1)	11.7 ± 0.6	28.4 ± 0.21	7.35
	Chloroform	23.1	–	7.5 ± 3.0	26.7 ± 1.0	13.0
	Acetonitrile	18.9	14.1	−2.0 ± 0.3	23.3 ± 0.10	17.5
$C_7H_9Fe(CO)_2I$	Xylene	(~8.2)	(~0.1)	10.7 ± 1.0	28.8 ± 0.36	2.71
	Benzene	8.2	0.1	3.1 ± 0.7	26.3 ± 0.26	2.69
	Di-n-butylether	3.9	19.2	20.0 ± 1.5	31.9 ± 0.53	3.45
	Chloroform	23.1	–	−1.1 ± 2.0	24.9 ± 0.56	3.60
	Nitrobenzene	14.8	4.4	−6.2 ± 1.8	23.0 ± 0.62	3.90
	Acetonitrile	18.9	14.1	−1.4 ± 1.4	24.0 ± 0.46	9.55
$C_9H_7Fe(CO)_2I$	Xylene	(~8.2)	(~0.1)	15.3 ± 0.6	30.5 ± 0.22	4.30

the solvent [11]. In all cases rigorous first-order kinetics were observed and concentration-dependence studies gave no evidence for any second-order contribution. All the compounds reported here undergo carbonyl substitution by a first-order dissociative mechanism as evidenced by the activation parameters given in Table III where the range of activation energies (23–30 Kcal mol^{-1}) and generally positive entropies are in the ranges expected for a dissociative mechanism.

In this work we have also prepared a series of monosubstituted η-cyclohexadienyl and η-cycloheptadienyl iron carbonyl halides by direct carbonyl substitution of the halide with a phosphite (or phosphine). The compounds so prepared are listed in Table I together with their infra-red carbonyl stretching frequencies. In general the phosphite substituted halides are more stable than the parent compounds and both the parent compounds and phosphite derivatives show a stability sequence with varying ring size as follows:

$$C_5H_5 > C_7H_9 > C_6H_7$$

The ν(C–O) infra-red stretching frequencies for the parent compounds lie in the sequence 2043, 2004, 2035, 2000; 2037, 2000 cm^{-1} which does not correlate with kinetic activity (see below). Substitution of a carbonyl group by a more weakly π-bonding phosphite or phosphine produces the expected downward shift in ν(C–O). In all the preparative experiments there was no evidence for the formation of ionic intermediates such as $[\eta\text{-Ring Fe(CO)}_2L]^+ I^-$ even in arene solvents such as benzene or xylene.

Effect of Ring Size

Table III shows that for xylene, the variation of rate with ring size is:

Cyclohexadienyl > Cycloheptadienyl >
Cyclopentadienyl

with activation energies lying in the sequence: Cyclohexadienyl ⩽ cycloheptadienyl < cyclopentadienyl whilst the entropies of activation for the three iodides are very similar. In strongly solvating media such as acetonitrile and nitrobenzene, the six-membered ring compound is again found to be more reactive than the seven-membered one although analogous data is not available for the five-membered compound in the same solvents. The above rate sequence suggests that ease of dissociation of the M–CO bond lies in the series

η-cyclohexadienylFe$(CO)_2I$ > η-cycloheptadienyl-Fe$(CO)_2I$ > η-cyclopentadienylFe$(CO)_2I$

but this is not in accord with the ν(C–O) stretching frequencies (Table I) which lie in the sequence cycloheptadienyl < cyclohexadienyl < cyclopentadienyl. The lack of correlation between reactivity and a ground state property such as ν(C–O) for a dissociative substitution reaction is a clear indication that the transitition state for the above reaction varies in structure depending on the size of the attached ring. This conclusion is further supported by the lower activation energy (by 4Kcal) of the indenyl compound compared with the analogous cyclopentadienyl compounds, as suggested originally by Mawby [5]. The solvent studies below provide further evidence for this conclusion.

Solvent Effects

In our previous studies of both the $Mn(CO)_5X$ (X = Cl, Br and I) [12] and $CpFe(CO)_2X$ (X = Br and I) [1] series, a general decrease in rate occurred on increase in solvent polarity and so it was concluded that the transition states were of similar structure and less polar than the ground state; indeed for the above series, good correlation between reactivity for a dissociative reaction and ground state properties such as ν(C–O) or (C–O) overlap populations was obtained [13]. Only one solvent, di-n-butyl ether, was anomalous and this was attributed to its acting as a coordinating solvent. For the six and seven-membered ring compounds the range of solvents has been extended considerably to include several with both donor and/or acceptor properties. The results are summarized in Tables II and III.

Unfortunately, it was not possible in this work to use n-octane as an "ideal" solvent because of both decomposition and low solubilities of the substrates and so xylene was chosen as a standard solvent of low dielectric constant (2.3), very poor donor and reasonably low acceptor qualities [11]. In the case of the cycloheptadienyl compounds the rate constants lie in the sequence:

$$k_{\mathrm{Benzene}} \sim k_{\mathrm{xylene}} < k_{\mathrm{DNB}} < k_{\mathrm{CHCl_3}} < k_{\mathrm{PhNO_2}} < k_{\mathrm{CH_3CN}}$$

while the sequence of activation energies is:

$$(E_a)_{\mathrm{DNB}} > (E_a)_{\mathrm{xylene}} > (E_a)_{\mathrm{C_6H_6}} > (E_a)_{\mathrm{CHCl_3}} > (E_a)_{\mathrm{CH_3CN}} > (E_a)_{\mathrm{PhNO_2}}$$

For the cyclohexadienyl case, the rates lie in the sequence:

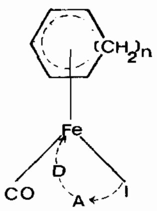
$$k_{\mathrm{xylene}} < k_{\mathrm{CHCl_3}} < k_{\mathrm{CH_3CN}}$$

and the activation energies in the sequence:

$$(E_a)_{\mathrm{xylene}} > (E_a)_{\mathrm{CHCl_3}} > (E_a)_{\mathrm{CH_3CN}}$$

These sequences are the opposite of those reported previously for the analogous cyclopentadienyl case and suggest a considerable change in structure of the transition state for the five-membered ring compounds compared to those for the six and seven-membered series both of which appear to have similar and *more* polar transition states in contrast to the *less* polar transition state of the five-membered ring systems.

The difference in polarity of transition states is further supported by approximate kinetic studies of the reaction of $CpFe(CO)_2Br$ and $P(OPh)_3$ in acetonitrile where a marked *decrease* in rate occurred in contrast to the 6 and 7 membered ring compounds. The above comprehensive solvent studies show not only the importance of the donor property of a solvent which leads to the well-known case of the solvent-assisted dissociative mechanism [14, 15] but also to the importance of mixed donor/acceptor properties in a given solvent [11]. In comparison with xylene, a solvent such as acetonitrile with comparable donor and acceptor numbers (14.1 and 18.9 respectively), leads to an increase in rate of carbonyl substitution, decrease in activation energy and markedly negative entropies of activation consistent with a more constrained transition state. We suggest that such effects are due to the solvent exerting a "push–pull" effect by coordinating in the usual way through its donor function at the vacant coordination site of the metal and by accepting electrons from the polarizable iodine atom through its acceptor function as shown below:



The results of Table II and III indicate that solvents such as nitrobenzene and acetonitrile can act in this way and even, apparently chloroform which through its acidic hydrogen atom can form hydrogen bonds with the iodine atom. The fact that the ratio $k_{\mathrm{CH_3CN}}/k_{\mathrm{xylene}}$ is greater for the seven-membered ring compound (3.52) than for the six-membered system (2.38) indicates that the push–pull mechanism is more important in the former case, whilst the lower rates of k_{CHCl_3}/k_{xylene} suggests further differences in the transition states of these systems. It follows, therefore that the transition states for the six and seven-membered ring complexes are of similar nature and more polar than the ground state in contrast to that for the cyclopentadienyl complexes and so correlation between reactivity and a purely ground state property such as ν(C–O) is unlikely for the complete series. The reasons for this change in polarity are not clear and we intend to use SCCCMO theory to compare the structures of both ground state and transition state in this sequence. It has been suggested that explicit repulsion between the CH_2 orbitals of the cyclohexadienyl ring and metal *d* orbitals is one factor leading to ring puckering in the parent cation [16]; it is possible that this effect may be relieved in the above transition states thereby leading to enhanced reactivity of the six and seven-membered ring systems compared to the cyclopentadienyl case. Theoretical studies of these compounds are in progress in our laboratories.

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