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INTERMEDIATES IN THE INTRAMOLECULAR LIGAND TRANSFER REACTIONS OF h^5-$C_5H_5Fe(CO)_2R$ COMPLEXES

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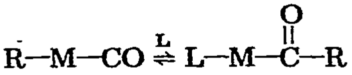
Summary

Dissolution of h^5-$C_5H_5Fe(CO)_2R$ (I) (R = cyclohexyl or cyclohexylmethyl) in DMSO leads to the formation of a solvent coordinated acyl complex, h^5-$C_5H_5Fe(CO)(COR)(DMSO)$ (II). Treatment of this complex with triphenylphosphine leads to its conversion to h^5-$C_5H_5Fe(COR)(PPh_3)$ (III). Rates for the reaction I ⇄ II and II → III have been determined. A comparison of the rates of the reaction I → III in eight solvents shows no specific rate acceleration in DMSO and no correlation with solvent donicity. The results are in accord with a two step mechanism in which the first intermediate is the coordinatively-unsaturated species h^5-$C_5H_5Fe(COR)(CO)$. The small spread in rates for solvents of widely different dielectric constants suggests little charge separation in the transition state for this step.

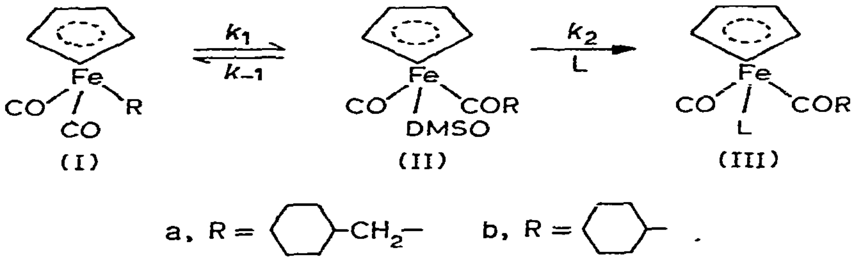
The effect of solvent on the rate of organometallic ligand transfer reactions of general form shown in eqn. 1 has been noted for several of these reactions



$$R{-}M{-}CO \overset{L}{\rightleftharpoons} L{-}M{-}\overset{\overset{O}{\|}}{C}{-}R \qquad (1)$$

[1, 2, 3], and it has been suggested that the specific coordinating power of the solvent is important in promoting these reactions [2, 3]. However, attempts to detect a solvent-coordinated intermediate in these reactions have been unsuccessful [2].

We wish to report detection of the first clearly defined solvent complex (II) as an intermediate in the ligand transfer reactions of I and to provide evidence that the rate of ligand transfer (I → III) in various solvents is unrelated to coordination ability of the solvent.



Dissolution of complex Ia or Ib in DMSO at room temperature results in a gradual color change from yellow to red. The IR spectra of these solutions show a progressive decrease in the intensity of the terminal carbonyl band at 2010 cm^{-1} concomitant with the appearance of a new peak at 1600 cm^{-1}. The latter absorption lies close to that observed for IIIa (L = CO, 1630 cm^{-1}; L = PPh_3, 1595 cm^{-1}) assignable to an acyl carbonyl fuction bound to the metal.

The reaction of Ia or Ib is also manifest in a decrease in the intensity of the cyclopentadienyl proton signal at τ 5.1 and the appearance of a new cyclopentadienyl singlet absorption at τ 5.33*. Additionally, new peaks appear at τ 7.25 (d, 2H, J = 6 Hz) for Ia and at τ 7.08 (br m) for Ib, corresponding to the protons adjacent to the acyl function in IIa and IIb. In IIIa and IIIb these protons absorb at τ 7.3 (L = CO, PPh_3) and at 7.4 (L = CO, PPh_3) respectively.

Specific coordination of the solvent in the intermediate (IIa) is evidenced by the appearance of two further singlet absorptions at τ 6.78 and 7.12 in the NMR spectrum of Ia when its reaction is followed in $CDCl_3$ solutions containing 30 mole % of DMSO. The integrated ratio of these signals to that at τ 5.3 is 3/3/5. These may be assigned to the two diasteriotopic methyl protons of coordinated DMSO.

The first order rate for the conversion of Ia to IIa in DMSO solvent was found to be 5.5×10^{-4} sec^{-1} at 37°. The equilibrium concentration, (IIa/Ia) is 0.71, from which $k_1^{37°} = 2.3 \times 10^{-4}$ sec^{-1} and $k_{-1}^{37°} = 3.2 \times 10^{-4}$ sec^{-1}.

Addition of triphenylphosphine to DMSO solutions of Ia, in which equilibrium has been attained, results in the disappearance of cyclopentadienyl proton resonance peaks corresponding to Ia and IIa and the appearance of the doublet (J = 1Hz) cyclopentadienyl peak corresponding to IIIa (τ 5.67).

When this reaction is carried out in the presence of a limited amount of triphenylphosphine** its rate is made sufficiently slow compared to the pre-equilibrium rate that k_2 may be determined. This was found to be 4.3×10^{-4} M^{-1} sec^{-1}.

Although a solvent coordinated intermediate is clearly generated in these reactions no specific rate acceleration is evident in dimethyl sulfoxide solution. This is indicated by a comparison of pseudo first order rate constants determined (Table 1) for the reaction of Ia with an eight-fold excess of PPh_3 in solvents of varying dielectric constant and coordinating power. These rates show no cor-

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* The h^5-Cp proton absorptions of IIIa and IIIb (L = PPh_3) are at τ 5.63 and 5.58 respectively, in $CDCl_3$.

** 20 mole % at the initial concentration of Ia. Maintenance of preequilibrium conditions could be independently checked during the reaction.

TABLE 1

RATE CONSTANTS FOR THE REACTION OF Ia WITH PPh_3 AT 37°

Solvent	$k_M \times 10^5$ (sec^{-1})	Solvent Donicity	$E_T(30)$
CH_3CN	5.9	14.1	46.0
CH_3SOCH_3	5.4[b]	29.8	45.0
CH_2Cl_2	3.6	*c*	41.1
CH_3COCH_3	2.5	17.0	42.2
$CH_3COOC_2H_5$	1.8	17.1	38.1
C_6H_6	1.7	0.1	34.5
THF[a]	1.4	20.0	37.4
heptane	1.3	< 0.1	30.9

[a] Tetrahydrofuran. [b] Rate constant (k_M) calculated from independently determined values of k_1, k_{-1}, and k_2 (eqn. 2) is 5.0×10^{-5} sec^{-1}. [c] No value available.

relation with solvent donicity [4]. A better, but by no means linear correlation is observed with such bulk solvent parameters as $E_T(30)$ values [5] derived from charge transfer energies of pyridinium phenol betaines. However, the small spread in rates for solvents of widely different dielectric constants and $E_T(30)$ values suggests a relatively small separation of charge in the rate limiting transition state.

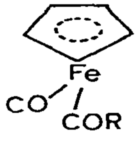
It has previously been shown [1a, b, 2, 3a, b] that the rates of ligand transfer reactions (eqn. 1) are not in general linear functions of phosphine concentration. These reactions conform instead to a two step mechanism (eqn. 2a or b).

$$[M] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [M'] \xrightarrow[L]{k_2} \text{product} \tag{2a}$$

$$[M] + (\text{sol}) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [M]\,(\text{sol}) \xrightarrow[L]{k_2} \text{product} \tag{2b}$$

$$k_M = [k_1 k_2 L/(k_{-1} + k_2 L)]M.$$

It has been suggested that the coordinating power of the solvent is important in promoting the first step of these reactions (eqn. 2b) [2, 3]. However, the lack of rate dependence in the reactions of I on solvent donicity is not in accord with such a mechanism. The results for I are better in accord with mechanism 2a, and suggest that the first intermediate [M'] in these reactions is the rearranged, coordinatively unsaturated species (IV). This intermediate reacts rapidly with phosphine, but in the presence of a solvent of high coordinating ability, such as DMSO, may be trapped.



(IV)

Experimental

All solvents were dried, stored over molecular sieves and degassed before use. NMR spectra were determined on a Varian A-60 spectrometer (purchased on NIH grant GM-13183-01) and absorption spectra were determined with a Perkin—Elmer Model 323 UV-visible spectrometer (purchased on NSF Development grant GU-3852).

Detection of complex IIa

Complex Ia (55 mg, 0.2 mmol) was dissolved in 0.3 ml of a 50% solution of DMSO in $CDCl_3$. The NMR spectrum was recorded after 1, 4 and 17 h, and the peaks at τ 5.33 (cp), 6.79 and 7.10 (Me) were integrated by weighing, since the DMSO peak prevented direct integration of the latter two absorptions. Equilibrium was reached within 4 h and the ratio of the integrated peaks, measured during this period and after 17 h, remained constant (5/3/3).

Kinetics. Determination of k_1, k_{-1} and k_2

A 0.6 *M* solution of Ia in DMSO-d_6 was made up in an NMR tube, and placed in the probe of the NMR spectrometer (37°). Reaction was followed by measuring the changes in intensity of both the cyclopentadienyl proton resonances of Ia and IIa with time. Measurements were taken every 5 min over 185 min. Equilibrium was attained in 2.5h ($K_{eq} = 0.71$). Least squares calculations gave values of $k = 5.40 \pm 0.03 \times 10^{-4}$ sec^{-1} ($r = 0.988$) and $k = 5.57 \pm 0.03 \times 10^{-4}$ sec^{-1} ($r = 0.992$), for the rate of reaction Ia $\rightleftarrows$ IIa.

After equilibrium had been reached, an amount of triphenylphosphine equivalent to 20 mole percent of the initial amount of Ia was added, and the increase in the intensity of the product peak at τ 5.67 was integrated every 5 minutes over a period of 140 min. During this period the intensity of the cyclopentadienyl proton peak of IIa remained essentially constant. Least squares calculations gave a value of $k_2 = 4.3 \pm 0.1 \times 10^{-3}\ M^{-1}$ min^{-1} ($r = 0.99$).

Determination of k_M

Both Ia and IIIa exhibit moderate absorption between 400-500 nm, with the greatest difference being at 460 nm. Solutions 0.025 *M* in Ia and 0.20 *M* in PPh_3 were made up and placed in 1 mm thermostatted pyrex or quartz cells. The change in density was followed continuously over two to seven half lives of reaction at 37°. Rates were calculated by least squares analysis, and correlation coefficients were greater than 0.99 for all experiments.

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