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# METALLOTROPIC REARRANGEMENT OF $\eta^5$-FLUORENYLTRICARBONYL MANGANESE IN ACID MEDIA

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## Summary

Using IR and PMR spectroscopy, it has been shown that on addition of trifluoroacetic acid to $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$ in $CH_2Cl_2$ solution protonation of position 9 of the fluorenyl ligand takes place with simultaneous migration of the metal atom onto the six-membered ring of the fluorenyl ligand, forming of $[(\eta^6\text{-}C_{13}H_{10})Mn(CO)_3]^+$.

## Introduction

In recent years, a great deal of attention has been given to metallotropic rearrangements in $\pi$-complexes, in which a change in the $\pi$-coordination position of the transition metal atoms occurs; for example, the migration of the metal atom from the five-membered ring to the six-membered one of indenyl ($C_9H_7$) or fluorenyl ($C_{13}H_9$) ligands. For such a rearrangement the valence state of the metal atom has to change.

In 1975, Treichel et al. [1] observed a $\eta^5 \rightarrow \eta^6$-type rearrangement in the complexes $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_9H_7)Fe$ and $(\eta^5\text{-}C_9H_7)_2Fe$ in acid media, resulting in $[(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_9H_8)Fe]^+$ and $[(\eta^5\text{-}C_9H_7)(\eta^6\text{-}C_9H_8)Fe]^+$, respectively. They assumed that the first step of this rearrangement was protonation at the transition metal atom with subsequent migration of the proton to the five-membered ring of the indenyl ligand and simultaneous transition of the iron atom to the six-membered ring. A reverse transition is possible by treatment with a base.

A rearrangement of the $\eta^5 \rightarrow \eta^6$ type is known to occur in the anion $[C_{13}H_9Cr(CO)_3]^-$ in the case of fluorenyl complexes [2,3]. Unlike the previous rearrangement, this one is reversible. In the $\eta^5$-form, the negative charge is localized at the chromium atom, while in the $\eta^6$-form it is localized at the $\pi$-ligand.

In 1977, Treichel and Johnson [4] observed that the cation of $\eta^6$-fluorene-

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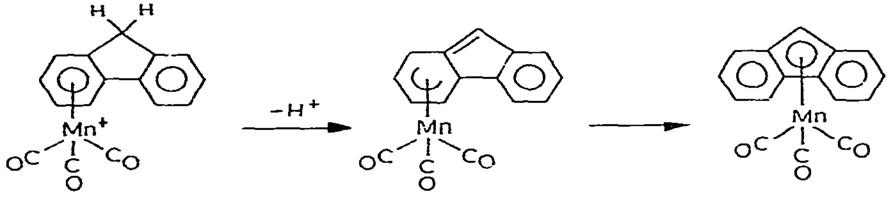
tricarbonylmanganese transforms to $\eta^5$-fluorenyltricarbonylmanganese on interaction with bases (e.g. triethylamine, tertiary potassium butylate). All three



(I) (II) (III) (1)

forms have been isolated and characterized by IR and PMR spectra. The I → II transition is fast, while the II → III transition is much slower. The authors pointed out that the reverse rearrangement from III to I in the presence of acids could not be achieved. They explain this by the lack of protonation at the metal atom because of the low basicity of the Mn atom in the $Mn(CO)_3$ group, making reference to one of our earlier works [5].

In the present work we found that the rearrangement from III to I does take place on addition to III of trifluoroacetic acid in a $CH_2Cl_2$ solution.

## Results and discussion

To examine the effect of the $\pi$-ligand on the basicity of the metal atom, we decided to check the capacity of $C_9H_7Mn(CO)_3$ and $C_{13}H_9Mn(CO)_3$ for protonation. In the case of $C_9H_7Mn(CO)_3$, no protonation was observed in the presence of $CF_3COOH$ in a $CH_2Cl_2$ solution. This observation was not unexpected in view of the earlier finding [6] that the rate of exchange of CO groups for $PPh_3$ in the series of complexes $LMn(CO)_3$ ($L = C_5H_5$, $C_9H_7$, $C_{13}H_9$) is virtually independent of the nature of L: i.e., the character of the Mn—CO bond in them is almost the same, which is why no substantial difference in the metal atom basicity is assumed to occur. However, unexpectedly for us and at variance with Treichel and Johnson's data [4], $C_{13}H_9Mn(CO)_3$ was found to interact with $CF_3COOH$. The interaction is accompanied by a high-frequency shift of the CO stretching bands of the initial complex III at 2018 and 1933 $cm^{-1}$, to 2077, 2062 and 2020 $cm^{-1}$ (Fig. 1).

The intensity ratio of the bands at 2077 and 2062 $cm^{-1}$ depends on the initial concentration of the complex and the complex/acid concentration ratio. We conducted a series of experiments to study the relationship between the intensity ratio of the bands at 2077 and 2062 $cm^{-1}$ and the complex and acid concentration. The protonation was carried out at a constant complex concentration 0.5 *M*) and at an increasing acid concentration (0.1 to 5 *M*), as well as at a constant complex/acid concentration ratio (1 : 20) and at increasing concentrations of the complex (0.02 to 0.1 *M*) and acid (0.4 to 2 *M*). In all cases we observed the same picture: as the complex and acid concentrations increase, immediately after preparation of the solution, the intensity of the band at 2077 $cm^{-1}$ in the IR spectrum becomes much greater than that of the band at 2062 $cm^{-1}$. When the solution is allowed to stand, the intensity of the band at 2062 $cm^{-1}$ gradually increases, and after approximately 30—60 min this band becomes more intense than that at 2077 $cm^{-1}$ (Fig. 1).

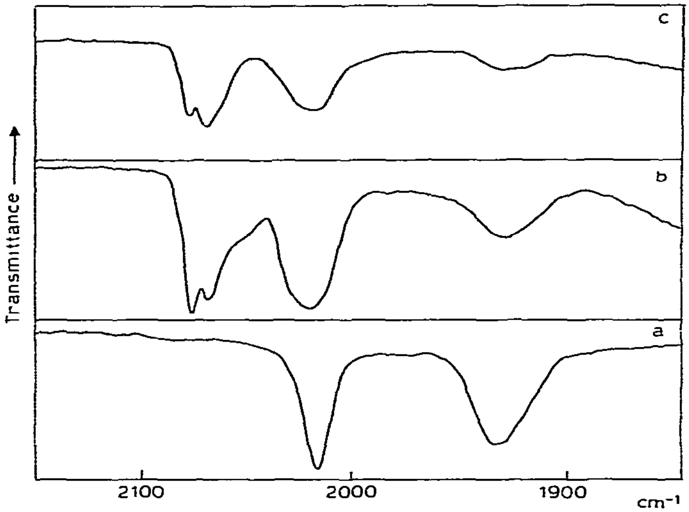


Fig. 1. IR spectra in the $\nu$(CO) region of $CH_2Cl_2$ solutions of: (a) ($\eta^5$-$C_{13}H_9$)$Mn(CO)_3$; (b) ($\eta^5$-$C_{13}H_9$)-$Mn(CO)_3$ + $CF_3COOH$ immediately after preparation of the solution; (c), (b) after an hour.

Thus, the reaction of III with $CF_3COOH$ yields at least two products. The rate of formation of the substance with $\nu$(CO) = 2077 $cm^{-1}$ is higher, however, than the increase in the intensity of the band at 2077 $cm^{-1}$ slows down, whereas the concentration of the substance with $\nu$(CO) = 2062 $cm^{-1}$ grows. Such a behaviour can be explained if it is assumed that the latter substance is derived from the former. At high concentrations and acidity, the high-frequency form accumulates at first, then partially transforms to the low-frequency one at a much slower rate. An alternative possibility is that the high-frequency form promotes the formation of the low-frequency one. As the reaction proceeds further, the intensity of the bands of the initial substance decreases but does not vanish completely. The absorption in the neighbourhood of 2020 $cm^{-1}$ is due to both the reaction products and the initial substance III. By resorting to computer-aided digital subtraction of the spectra and normalizing the subtraction over the band at 1933 $cm^{-1}$ belonging to III, we have shown that the absorption with a maximum at 2020 $cm^{-1}$ has a contribution of the reaction products.

In order to identify the reaction products we carried out a separation of the reaction mixture. After removal of the solvent and acid and dissolution of the solid residue in acetone, the high-frequency form was precipitated in the form of the tetrafluoroborate. The low-frequency form cannot be separated as a salt. It remains in solution and dissolves in benzene after the solution is evaporated. The IR spectra of both substances in the region of the $\nu$(CO) vibrations are illustrated in Fig. 2, while the PMR spectrum of the high-frequency form is presented in Table 1. Analysis of the spectra of the high-frequency form indicates that it represents $[(\eta^6\text{-}C_{13}H_{10})Mn(CO)_3]^+BF_4^-$ (compound I). This is corroborated by the arguments below.

The IR spectrum exhibits two intense bands in the $\nu$(CO) region, at 2077 and

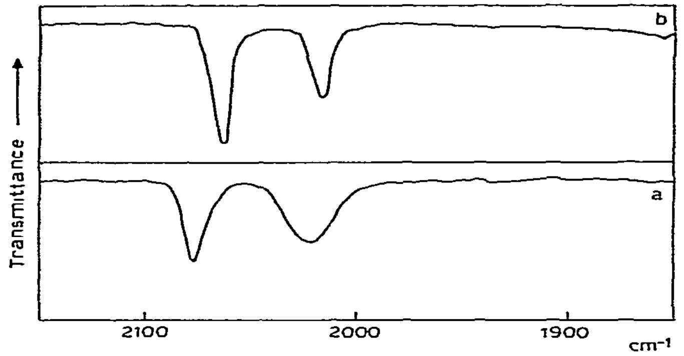


Fig. 2. IR spectra in the $\nu$(CO) region of form I(a) and form IV(b) in $CH_2Cl_2$ solution.

2024 $cm^{-1}$, whose intensity ratio and shape are typical of the $M(CO)_3$ group. Their frequencies are 60—90 $cm^{-1}$ higher as compared to the initial compound III, which is indicative of an increase in the formal positive charge at the metal atom. Addition of $Et_3N$ to a solution of I in $CH_2Cl_2$ brings about changes in the spectrum, similar to those observed during deprotonation of I [4]. The bands at 2077 and 2024 $cm^{-1}$ disappear, giving way to those at 2032, 1965, and 1952 $cm^{-1}$. Treichel and Johnson [4] ascribed these bands to the product II. When the solution is allowed to stand these bands gradually diminish in intensity, and bands at 2018 and 1933 $cm^{-1}$ belonging to $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$ (III) appear instead. In the work cited here [4], the II → III transition is accelerated by conducting the reaction in boiling hexane. We studied this reaction at room temperature, and the formation of III was clearly detected by the differential spectroscopy method (Fig. 3).

The PMR spectrum is identical to that [4] for $[(\eta^6\text{-}C_{13}H_{10})Mn(CO)_3]^+$. The signals observed in it are typical of two non-equivalent benzene rings (coordinated and uncoordinated) as well as of the $CH_2$ group in the five-membered

TABLE 1

PMR SPECTRA OF FLUORENYL COMPLEXES OF Mn IN $(CD_3)_2CO$ SOLUTION

| Substance | Non-coordinated six-membered ring | Coordinated six-membered ring | Five-membered ring |
|---|---|---|---|
| $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$ | 8.29 (d)<br>7.62 (d)<br>7.32 (t)<br>7.29 (t) | | 5.92 (s) |
| $(\eta^6\text{-}C_{13}H_{10})Mn(CO)_3BF_4$ | 8.23 (d,7.6) [a]<br>7.82 (d,7.6)<br>7.71 (t,7.6)<br>7.64 (t) [b] | 7.59 (d) [b]<br>7.53 (d,6.5)<br>7.01 (t,5.4)<br>6.81 (t,5.4) | 4.53,AB(23.8) |

[a] Multiplicity and J in Hz in parentheses. [b] Because of overlap of the signals corresponding to the protons of the coordinated and non-coordinated rings and the fluorene impurity, the data from Ref. 4 were used for assignment.

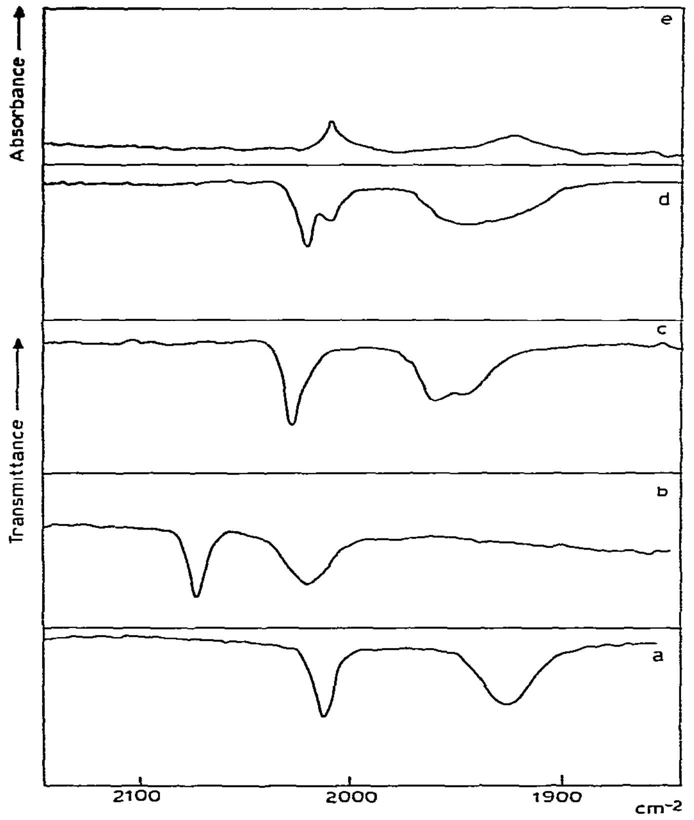


Fig. 3. IR spectra in the $\nu$(CO) region of $CH_2Cl_2$ solutions of: (a) ($\eta^5$-$C_{13}H_9$)Mn(CO)$_3$; (b) [($\eta^6$-$C_{13}H_{10}$)-Mn(CO)$_3$]$^+$; (c) (b) + $Et_3N$ immediately after addition of $Et_3N$; (d) (c) after 12 hours; (e) difference spectrum of (d)—(c) ($\eta^5$-$C_{13}H_9$)Mn(CO)$_3$.

ring (AB system). The data are presented in Table 1 together with the spectrum of the initial compounds III.

Thus, it can be considered proved that when III is acted upon by $CF_3COOH$ in a $CH_2Cl_2$ solution, compound I or the $\eta^6$-product of metallotropic rearrangement is formed.

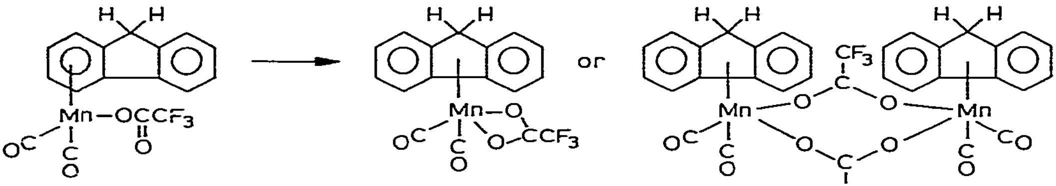
Treichel and Johnson [4] failed to observe this rearrangement, probably because of the insufficient concentration of the acid. In view of the low basicity of the Mn atom in tricarbonyl complexes, it may be assumed that the protonation in the presence of an acid proceeds directly on the five-membered ring of the fluorenyl ligand, causing rearrangement of the metal atom onto a six-membered ring. This does not necessarily mean that the protonation on the ring must be preceded by protonation at the metal atom.

We also noticed that in the case of the monophosphine derivative of III, ($\eta^5$-$C_{13}H_9$)Mn(CO)$_2$PPh$_3$, in which the basicity of the metal atom is increased due to the presence of the electron-donating triphenylphosphine ligand, $CF_3COOH$ causes protonation at the metal atom without any transfer of the proton onto the ring and metallotropic rearrangement. The results of the protonation studies of the complexes $LMn(CO)_2PPh_3$ ($L = C_5H_5, C_9H_7, C_{13}H_9$) will be published elsewhere.

The structure of the low-frequency form (compound IV) resulting from the reaction is not yet clear. It is known that the formation of IV is preceded by the appearance of complex I in the solution. IV is not precipitated by the $BF_4^-$ ion, dissolves in nonpolar solvents, and seems to be a substance other than a salt. In the presence of $Et_3N$ it does not transform to the initial III, and it does not interact with $CF_3COOH$. The IR spectrum of solid IV shows two bands of metal—carbonyl groups, each band being split into a doublet (2075, 2060, 2017, 2010 $cm^{-1}$), highly intense bands at 1189 and 1152 $cm^{-1}$ (stretching vibrations of C—F in the $CF_3$ group), and bands at 1683 and 1413 $cm^{-1}$ (asymmetric and symmetric vibrations of the carboxyl in the trifluoroacetate group). In $CH_2Cl_2$ solution only two bands at 2062 and 2011 $cm^{-1}$ were observed in the $\nu(CO)$ region, the first band being much stronger, whereas the half-widths of both bands were almost the same. Such a spectrum is not typical of the $M(CO)_3$ group and looks more like the spectrum of the $M(CO)_2$ group in which the M—CO bonds form an angle less than 90° [7].

IV is presumably the product of substitution of one of the CO groups in complex I by the trifluoroacetate ligand (IVa). Such a substitution may be promoted by the positive charge at the Mn atom in I. The frequencies of the symmetric and asymmetric vibrations of the carboxyl are spaced 270 $cm^{-1}$ apart, which suggests that either there is a bidentate coordination of the trifluoroacetate ligand (IVb) or the complex is binuclear with bridged carboxyl groups (IVc).

The structures IVb and IVc may form from IVa, and for the 18-electron shell of the Mn atom to be retained migration of the latter back onto the five-membered ring, is supposed to occur.



(IVa) (IVb) (IVc)

In complexes IVb and IVc the Mn atom contains, in addition to the π-ligand, four substituents in its coordination sphere. This must result in decrease of the angle between the M—CO bonds, which approaches 90° in the $M(CO)_3$ group. Hence, the above-mentioned change in the intensity ratio of the symmetric and asymmetric stretching vibrations of the CO group at the metal atom may take place.

## Experimental

The IR spectra were recorded on a Bruker infrared Fourier transform IFS-113V spectrometer, interfaced with an Aspect 2000 computer. The solutions were prepared under an argon atmosphere. The resolution was 2 $cm^{-1}$.

The PMR spectra were measured on a Bruker NMR spectrometer, model WH-360, with an operating frequency of 360 MHz.

$\eta^5$-$C_{13}H_9Mn(CO)_3$ was purified by repeated chromatography on $Al_2O_3$ and recrystallization from pentane, m.p. 119—120°C (118—119°C [8]). The purity of the substance was checked by thin-layer chromatography on $SiO_2$. $CF_3COOH$ and $CH_2Cl_2$ were distilled under argon. The preparation of solutions for spectroscopic measurements and filling of the cells were also carried out under pure argon.

0.41 g (1.35 mmol) of $C_{13}H_9Mn(CO)_3$ were dissolved in a mixture of 4.2 ml (56.1 mmol) of $CF_3COOH$ and 14 ml of $CH_2Cl_2$. The solution was allowed to stand at 20°C until equilibrium was reached. The process was monitored by IR spectroscopy. After several hours, the solvent and acid were evaporated, the residue was dissolved in 8 ml of acetone, and a solution of 0.20 g (1.9 mmol) of $NH_4BF_4$ in 2 ml of water was added. Then, 20 ml of ethyl ether were added, and the precipitate was filtered off. This step was repeated four times. The residues were blended and dried in vacuum over $CaCl_2$, then washed with three portions of benzene and extracted several times with $CH_2Cl_2$. The solution in $CH_2Cl_2$ was concentrated by evaporation to a small volume and cooled until crystals precipitated. The resulting pale yellow substance was moderately soluble in $CH_2Cl_2$ and insoluble in benzene. $\nu(CO)(CH_2Cl_2)$ 2077, 2024 $cm^{-1}$ (complex I).

Acetone/ether mother liquors were evaporated to dryness, and residue was dissolved in benzene, with separation of a certain amount of water. The benzene solution was dried over $CaCl_2$ and concentrated by evaporation. The residue was extracted several times with hexane. The solution in hexane contained the initial $\eta^5$-$C_{13}H_9Mn(CO)_3$; $\nu(CO)(CH_2Cl_2)$ 2018, 1933 $cm^{-1}$.

The residue from the extraction with hexane was a bright yellow substance soluble in benzene and poorly soluble in hexane; $\nu(CO)$ $(CH_2Cl_2)$ 2062, 2011 $cm^{-1}$ (complex IV).

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