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METALLOTROPIC $\eta^5 \to \eta^6$ REARRANGEMENT IN INDENYLTRICARBONYL COMPLEXES OF MANGANESE AND RHENIUM IN AN ACID MEDIUM

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Summary

An IR spectroscopic study has shown that the reactions of $(\eta^5\text{-}C_9H_7)M(CO)_3$ (M = Mn, Re) and $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$ with $AlCl_3 \cdot HCl$ and FSO_3H involve metallotropic $\eta^5 \to \eta^6$ rearrangement in which the metal carbonyl group migrates from the five- to the six-membered ring of the aromatic ligand. The reverse $\eta^6 \to \eta^5$ rearrangement is initiated by bases.

In a previous investigation we demonstrated that, when η^5-fluorenylmanganese tricarbonyl is treated with trifluoroacetic acid, a metallotropic rearrangement takes place, with the metal carbonyl fragment being transferred from the five- to the six-membered ring of the planar π-aromatic ligand [1].

η^5-Indenyl complexes of manganese and rhenium do not react with trifluoroacetic acid because the indenyl ligand is less basic than the fluorenyl one. However, it might be expected that indenyl complexes would react with stronger acids.

Thus, an IR spectroscopic study was made on the reaction of η^5-indenyltricarbonyl complexes of manganese and rhenium $(\eta^5\text{-}C_9H_7)M(CO)_3$ (M = Mn, Re), as well as on η^5-fluorenylmanganese tricarbonyl, $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$, with the acids $AlCl_3 \cdot HCl$ and FSO_3H, and it was found that these acids cause migrations of the metal carbonyl group from the five- to the six-membered ring of the indenyl or fluorenyl ligand. When the resulting η^6-cations are treated with a base, the reverse $\eta^6 \to \eta^5$ rearrangement takes place.

Results and discussion

When an acid is added to a solution of $(\eta^5\text{-}C_9H_7)Mn(CO)_3$ (I) in methylene chloride or benzene, in the IR spectrum of the solution the intensities of the ν(CO) bands at 2020 and 1935 cm^{-1} (corresponding to the initial complex) decrease, and two pairs of new ν(CO) bands appear at 2074, 2013 and 2048, 1975 cm^{-1}. These bands are shifted into the high-frequency region of the spectrum, as compared to the ν(CO) bands of the initial complex, and can be ascribed to two different products of the reaction between complex I and the acid (Fig. 1). A similar picture is observed in the case of (η^5-$C_{13}H_9$)Mn(CO)$_3$ (III) (Fig. 2), whereas in the case of (η^5-C_9H_7)Re(CO)$_3$ (II) bands corresponding to only one product, associated with higher ν(CO) frequencies, appear in the spectrum (Fig. 1).

The relative amounts of the reaction products depend on the nature of the complex and the acid, besides the rates of their formation being different. The values of ν(CO) for the initial complexes and the reaction products are listed in Table 1.

The rate of formation of product **B** is higher than that of product **A**, the intensity of the band at 2074 cm^{-1} increasing rather slowly. When complex I reacts with $AlCl_3 \cdot HCl$, the amount of product **B** in the reaction mixture exceeds that of product **A**; complex II does not yield product **B**; and the reaction of complex III with $AlCl_3 \cdot HCl$ yields both products in roughly the same amounts.

Only manganese complexes react with fluorosulfonic acid, while the rhenium complex decomposes under the same conditions. Manganese complexes yield product **B** only at the initial moment of the reaction, after which the bands at 2048 and 1975 cm^{-1} rapidly disappear and a new band appears at 2056 cm^{-1} with the bands

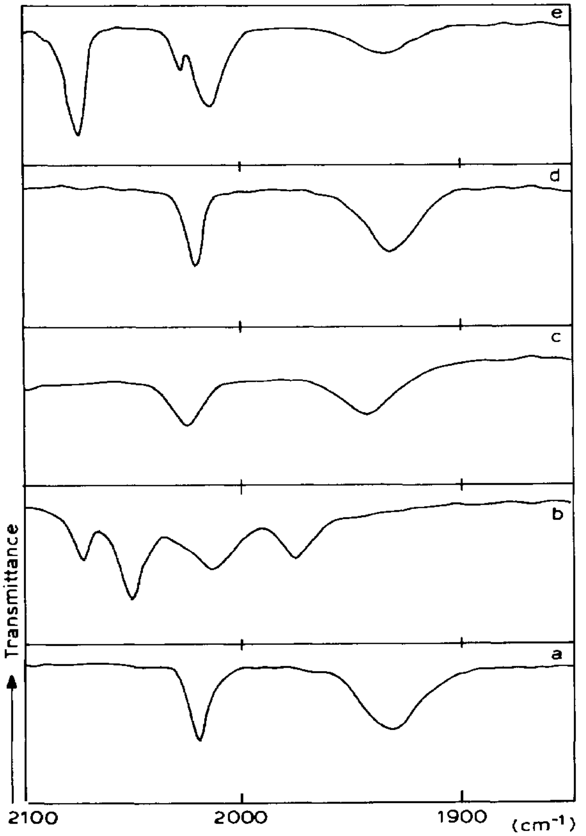


Fig. 1. IR spectra in the ν(CO) region of a CH_2Cl_2 solution of: (a) (η^5-C_9H_7)Mn(CO)$_3$; (b) (a)+$AlCl_3\cdot$HCl; (c) (b)+Et_3N; (d) (η^5-C_9H_7)Re(CO)$_3$; (e) (d)+$AlCl_3\cdot$HCl.

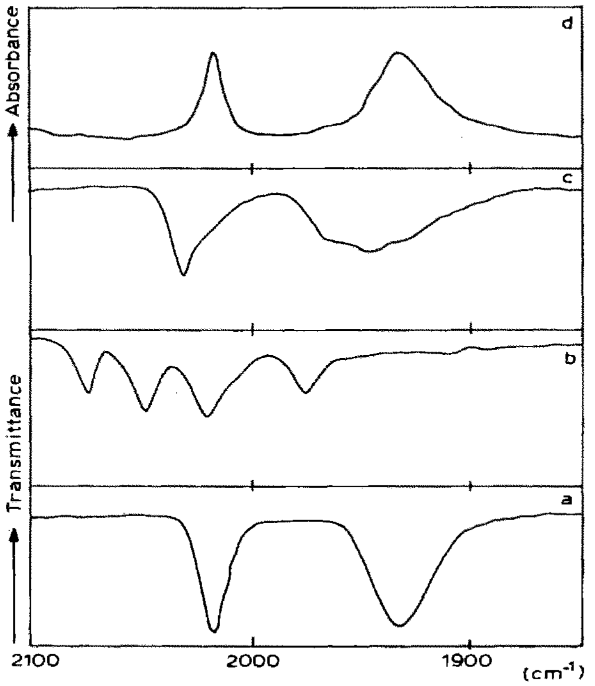


Fig. 2. IR spectra in the ν(CO) region of a CH_2Cl_2 solution of: (a) (η^5-$C_{13}H_9$)Mn(CO)$_3$; (b) (a)+$AlCl_3\cdot HCl$; (c) (b)+Et_3N; (d) spectrum (c) subtracted from that of solution (c) after the latter was allowed to stand for 12 h; the subtraction was done on a computer.

of product **A** remaining in the IR spectrum. The band at 2056 cm^{-1} does not disappear when a base is added to the solution and it seems to belong to the product of substitution of the CO groups or the product of decomposition. When the concentration of FSO_3H is increased, product **B** is not observed in the IR spectrum at all, and only the bands corresponding to product **A** and to the decomposition product can be seen.

Analysis of the experimental data suggests that in all cases product **A** results from a metallotropic $\eta^5 \rightarrow \eta^6$ rearrangement. This is shown by the following results: in the case of complex III, ν(CO) of product **A** are the same as in the case of (η^6-$C_{13}H_{10}$)Mn(CO)$_3$ which was obtained in the previous work [1] in the presence of CF_3COOH and whose structure was definitively established by IR and PMR spectroscopy. When acid solutions of the fluorenyl complex are treated with Et_3N, the bands corresponding to both products disappear, and three new bands appear in

TABLE 1

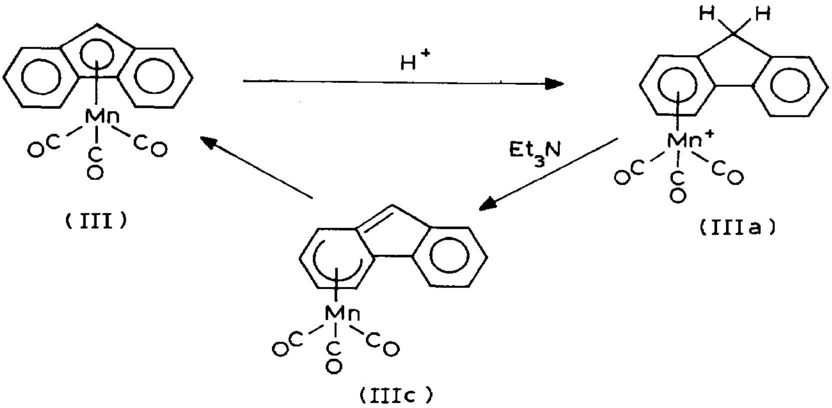
ν(CO) (cm^{-1}) OF INDENYL AND FLUORENYL COMPLEXES OF Mn AND Re AND THE PRODUCTS OF THEIR REACTION WITH ACIDS IN A CH_2Cl_2 SOLUTION [a]

Compound	Initial complex	Product **A**	Product **B**
(η^5-C_9H_7)Mn(CO)$_3$ (I)	2020, 1935	2074, 2013	2049, 1975
(η^5-C_9H_7)Re(CO)$_3$ (II)	2023, 1925	2074, 2007	–
(η^5-$C_{13}H_9$)Mn(CO)$_3$ (III)	2018, 1933	2076, 2020	2048, 1976

[a] The frequencies are the same for the products of the reaction with $AlCl_3\cdot HCl$ and FSO_3H.

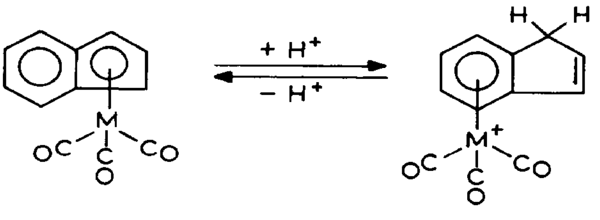
the spectrum at 2032, 1962 and 1950 cm^{-1}, similar to those observed in previous experiments [1,2] and associated with the deprotonated complex IIIc, which slowly transforms into the initial complex III. The emergence of the latter in the mixture is clearly seen in the differential IR spectrum produced by computer-aided subtracted (Fig. 2). Thus, under the effect of $AlCl_3 \cdot HCl$ and FSO_3H, as well as CF_3COOH, the five-membered ring in complex III undergoes protonation with simultaneous $\eta^5 \rightarrow \eta^6$ rearrangement of the metal carbonyl group. During deprotonation in the presence of a base, the reverse $\eta^6 \rightarrow \eta^5$ rearrangement involves the formation of a stable complex IIIc (Scheme 1).

SCHEME 1



The IR spectra recorded after $AlCl_3 \cdot HCl$ was added to solutions of complexes I and II, and FSO_3H was added to a solution of complex I, also feature bands at 2074 and 2010 cm^{-1} (product A), which can be ascribed, by analogy with complex III, to the η^6-indenyltricarbonyl cation. However, when a base is added to these solutions, the bands at 2074 and 2010 cm^{-1} disappear, giving way to those corresponding to the initial complex; that is, the intermediate deprotonated form is not stable as in the case of the fluorenyl complex. This is completely consistent with the hypothesis that complex IIIc is stabilized as a result of redistribution of the electron density throughout the fluorenyl ligand, whereas such delocalisation in the indenyl ligand is less probable.

It can be assumed, by analogy with the $\eta^5 \rightarrow \eta^6$ rearrangement studied in experiments with η^5-fluorenylmanganese tricarbonyl, that product A obtained by the reaction of complexes I and II with acids comprises essentially η^6-indene complexes of manganese and rhenium which have not been described before and which are not formed in the reaction of the corresponding η^5-complexes with trifluoroacetic acid. The process can be represented as follows:



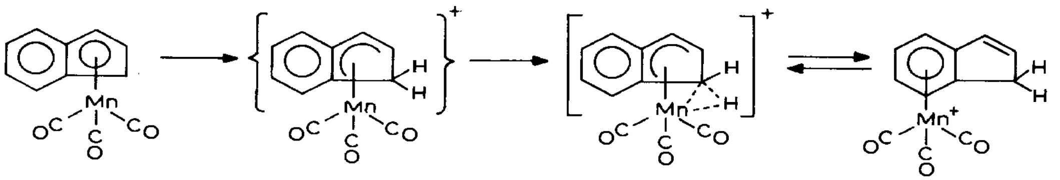
(M = Mn, Re)

To verify this hypothesis, we resorted to counter-synthesis; a borofluoride of η^6-indenemanganese tricarbonyl was obtained. In the IR spectrum of this salt, bands at 2074 and 2013 cm^{-1} were observed in the ν(CO) region, which disappear under the effect of Et_3N, being replaced by bands at 2020 and 1935 cm^{-1} associated with complex I.

Thus, when complexes I and II are treated with acids, metallotropic $\eta^5 \rightarrow \eta^6$ rearrangement unknown for such complexes takes place. It is associated with migration of the metal carbonyl group from the five- to the six-membered ring of the indenyl ligand.

As can be inferred from the foregoing, apart from being involved in metallotropic rearrangement, in acid medium complexes I and III yield another substance (product **B**). The frequencies corresponding to this substance are 30 to 40 cm^{-1} above those corresponding to the initial η^5-complex and lower than those in the case of the η^6-form. The experimental results suggest that substances **B** are products of the reversible interaction of complexes I and III with the proton, in view of the fact that they are readily deprotonated in the presence of bases so that the initial complexes are formed. The deprotonation of the **B** form proceeds more easily than that of the **A** form with the corresponding bands being the first to disappear. Significantly, in the case of IIIb, deprotonation directly results in complex III rather than IIIc. The implication is that the metal in IIIb is linked with the five-membered ring. The small shift of the ν(CO) frequencies in the case of the **B** form undermines the hypothesis that the protonation occurs at the metal atom because, should the latter be the case, the frequency shifts would have been more pronounced (100–150 cm^{-1}) [3]. Interaction of the proton with the CO groups is also excluded because it would have resulted in different changes in the ν(CO) region of the spectrum, namely, in the decrease of the frequency of one of the bands and an increase, or perhaps splitting, of that of the other [3]. Another possible hypothesis postulates the formation of a complex with a hydrogen bond prior to protonation and metallotropic rearrangement. Supporting this hypothesis are the small ν(CO) shift associated with a minor decrease of the electron density at the metal atom, and the reversibility of the interaction. An experiment with dilution was carried out to verify the hypothesis. The original assumption was that strong dilution would break the hydrogen bond and ν(CO) bands corresponding to the initial complex would appear in the IR spectrum. However, after strong (30-fold) dilution, the bands at 2048 and 1975 cm^{-1} did disappear but no ν(CO) bands corresponding to the initial complex I emerged instead, and the optical density of the band at 2074 cm^{-1} increased – that is, strong dilution forces product **B** to transform into product **A**.

The above results suggest that the proton is most probably attached to the five-membered ring of the aromatic ligand and the resulting electron-deficient 17-electron complex is stabilized either by migration of the metal into the six-membered ring (form **A**) or by formation of a bridged three-centre, two-electron bond (form **B**).



(I) (Ib) (Ia)

The formation of complexes of the **B** type as a result of protonation of butadieneiron tricarbonyl complexes [4,5], as well as that of η^4-cyclohexadienemanganese tricarbonyl [6], has been described. These are rather stable compounds, and their ν(CO) frequencies are 20 to 30 cm^{-1} above those of the unprotonated complexes. The bridged hydrogen is highly acidic and readily detaches itself in the presence of bases. The available experimental data do not contradict structure Ib, although additional experiments are to be conducted for its corroboration.

Experimental

All reactions were conducted in an inert atmosphere. Dehydrated solvents that had been distilled in Ar were used. $AlCl_3$ had not been sublimated because no reaction is observed with dry sublimated $AlCl_3$. The complexes seem to react with the acid $AlCl_3 \cdot HCl$ resulting from hydrolysis of wet $AlCl_3$. Complexes $(\eta^5\text{-}C_9H_7)Mn(CO)_3$, $(\eta^5\text{-}C_9H_7)Re(CO)_3$, and $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$ were prepared by the method of Kolobova et al. [7].

A mixture of the complex (1 mmol) and $AlCl_3$ (2 mmol) was stirred at 20°C in CH_2Cl_2, and IR spectra were taken of the reaction mixture. The same products **A** and **B** are formed both when gaseous HCl is passed through the solution and when the complex is added to a solution of $AlCl_3 \cdot HCl$ prepared in advance.

Formation of $(\eta^6\text{-}C_9H_8)Mn(CO)_3{}^+\ BF_4{}^-$

0.5 g (1.8 mmol) of $Mn(CO)_5Br$, 1.75 g (1.65 mmol) of freshly distilled indene and 0.45 g (3.4 mmol) of $AlCl_3$ were boiled in 100 ml of hexane for 3 h. After being cooled, the reaction mixture was poured into 100 ml of chilled water, and the organic layer was extracted with water (2 × 25 ml). The aqueous layer was filtered, 0.19 g (1.8 mmol) of NH_4BF_4 was added, and the whole was evaporated dry. The IR spectrum of the solution of the residue in CH_2Cl_2 revealed the presence of product **A**. From the organic layer, after evaporation and chromatography on Al_2O_3, 0.16 g of $Mn_2(CO)_{10}$, identified by TLC and IR spectroscopy, was isolated.

The IR spectra were recorded on a Specord IR-75 spectrophotometer as well as on Bruker IFS-113v and Bruker IFS-45 Fourier-transform spectrometers. The resolution was 2 cm^{-1}.

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