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# INTERACTION OF CYCLOPENTADIENYL CARBONYL PHOSPHINE COMPLEXES OF MANGANESE WITH LEWIS ACIDS.

## INFRARED SPECTRA*

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## SUMMARY

From IR-spectroscopic studies it is shown that phosphine derivatives of cyclopentadienylmanganese tricarbonyl interact reversibly with $SnCl_4$ and another Lewis acids in $CH_2Cl_2$ solution. The structures of the resulting complexes are discussed. Complex formation is favoured as the electron-donor properties of both the $\pi$-ring substituents and of the phosphine ligands attached to manganese atom are increased. The ability of Lewis acids to undergo such complex formation follows the series: $SnCl_4 > SbCl_3 > HgCl_2 > GeCl_4$.

## INTRODUCTION

In previous papers in this series[1-3] it has been shown that the complexes $ArCr(CO)_2L$ and $CpMn(CO)_2L$ (where $Ar = C_6H_6$ or substituted benzenes, Cp = $\pi$-cyclopentadienyl and L = tertiary phosphines) undergo reversible protonation when treated with $CF_3COOH$ in $CH_2Cl_2$. Using $^1H$ NMR spectroscopy, it has been shown that with the chromium complexes[2] the proton adds at the metal atom. From this result it is evident that replacement of a CO by a tertiary phosphine in the $M(CO)_3$ group should markedly increase the basicity of the metal and make proton addition possible. Thus it would seem quite reasonable to suggest that compounds of the type $ArCr(CO)_2L$ and $CpMn(CO)_2L$ should also react in a similar manner with other electrophilic agents, *e.g.* aprotic acids. This study is concerned with reactions of compounds of the type $CpMn(CO)_2L$ (I) and $CpMn(CO)L_2$ (III) with $SnCl_4$ and other Lewis acids in $CH_2Cl_2$ solution studied by means of infrared spectroscopy.

The formation of adducts between transition metal carbonyl complexes and Lewis acids has been reported repeatedly (see review ref. 4). Solid adducts of Lewis acids containing elements in Groups IIB (Zn, Cd, Hg) and IIIB (B, Al, Ga, In) of the Periodic Table have been described[4]. However, interaction between a transition metal carbonyl complex and a Lewis acid containing an element in Groups IV or V has been little studied.

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* Part V of the series: Protonation of metal carbonyl complexes.

TABLE 1

THE FREQUENCIES OF CO STRETCHING MODES ($cm^{-1}$) FOR COMPLEXES OF FORMULA $CpMn(CO)_2L$ IN $CH_2Cl_2$ SOLUTION IN THE PRESENCE OF $SnCl_4$

| *No.* | *Formula* | *Without $SnCl_4$* | *In the presence of an equimolar amount of $SnCl_4$* | | *In the presence of excess $SnCl_4$* | |
|---|---|---|---|---|---|---|
| | | | *(I)* | *(II)* | *(I)* | *(II)* |
| 1 | $C_5H_5Mn(CO)_3$ | 1935, 2025 | 1935, 2025 | | 1935, 2025 | |
| 2 | $C_5H_5Mn(CO)_2P(OPh)_3$ | 1900, 1965 | 1900, 1965 | | 1900, 1965 | 2002, 2045 |
| 3 | $C_5H_5Mn(CO)_2PPh_3$ | 1870, 1937 | 1870, 1937 | 1995, 2035 | | 1995, 2035 |
| 4 | $C_5H_5Mn(CO)_2AsPh_3$ | 1870, 1935 | 1870, 1935 | 1984, 2023 | | 1993, 2032 |
| 5 | $C_5H_5Mn(CO)_2SbPh_3$ | 1870, 1934 | 1870, 1934 | 1984, 2022 | | 1984, 2022 |
| 6 | $C_5H_5Mn(CO)_2P(C_6H_4CH_3\text{-}p)_3$ | 1867, 1933 | 1867, 1933 | 1992, 2023 | | 1992, 2033 |
| 7 | $C_5H_5Mn(CO)_2P(C_6H_4OCH_3)_3$ | 1865, 1933 | 1865, 1933 | 1990, 2032 | | 1990, 2032 |
| 8 | $C_5H_5Mn(CO)_2P(i\text{-}C_3H_7)_3$ | 1856, 1925 | 1856, 1925 | 1962, 2043 | | 1962, 2043 |
| 9 | $C_5H_5Mn(CO)_2P(C_6H_{11})_3$ | 1853, 1924 | 1853, 1924 | 1960, 2042 | | 1960, 2042 |
| 10 | $Et_5C_5Mn(CO)_3$ | 1918, 2007 | 1918, 2007 | 2074 | 1918, 2007 | 2074 |
| 11 | $Et_5C_5Mn(CO)_2PPh_3$ | 1850, 1918 | 1850, 1918 | 1946, 2027 | | 1946, 2027 |

## RESULTS AND DISCUSSION

The CO stretching modes of the various compounds investigated in $CH_2Cl_2$ solution are given in Tables 1 and 2. The compounds of formula $CpMn(CO)_2L$ (I) exhibit two bands for $\nu(CO)$ which may be attributed to the symmetric and antisymmetric CO modes of $A'$ and $A''$ species respectively. If solutions of $SnCl_4$ in $CH_2Cl_2$ or pure $SnCl_4$ are added to the solutions of (I) in the same solvent, the colour changes instantly from yellow to red or dark brown, with the solution ultimately becoming turbid and leading in some cases to precipitation of a solid. In such cases the solution over the solid exhibited two new bands shifted by 80–110 $cm^{-1}$ towards higher wave numbers in addition to $\nu(CO)$ of the starting compounds. Qualitative analysis of the spectrum showed that the intensity ratio of bands due to the starting compounds and the new bands depends both on the nature of the ligand L and on the

TABLE 2

THE FREQUENCIES OF CO STRETCHING MODES ($cm^{-1}$) FOR COMPLEXES OF FORMULA $CpMn(CO)L_2$ IN $CH_2Cl_2$ SOLUTION IN THE PRESENCE OF EXCESS APROTIC ACIDS (Y)

| *No.* | *Formula* | *In $CH_2Cl_2$* | | | | *In $CH_2Cl_2$/THF* | |
|---|---|---|---|---|---|---|---|
| | | *Without Y* | *$SnCl_4$* | *$GeCl_4$* | *$SbCl_3$* | *Without $HgCl_2$* | *$HgCl_2$* |
| 12 | $C_5H_5Mn(CO)(Ph_2PCH_2PPh_2)$ | 1842 | 1942 | Decomp. | 1940 | 1850 | 1938 |
| 13 | $C_5H_5Mn(CO)(Ph_2PCH_2CH_2PPh_2)$ | 1840 | 1935 | 1840 and 1935[a] | 1936 | 1847 | 1930 |
| 14 | $C_5H_5Mn(CO)(Ph_2PCH_2CH_2CH_2PPh_2)$ | 1825 | 1920 | 1825 and 1920[a] | 1918 | 1833 | 1920 |
| 15 | $C_5H_5Mn(CO)(PPh_3)_2$ | 1827 | 1923 | 1827 and 1940[b] | 1924 | 1834 | 1920[b] |

[a] Equilibrium shifted towards the starting materials. [b] Rapid decomposition.

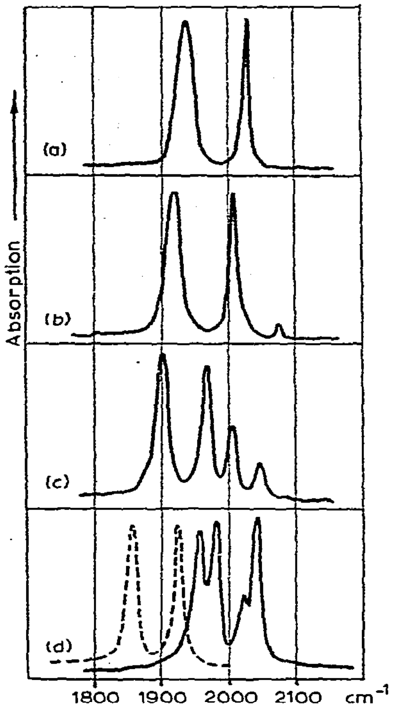

Fig. 1. The CO stretching mode region of the IR spectra for $CH_2Cl_2$ solutions of the following complexes in the presence of excess $SnCl_4$: (a) $C_5H_5Mn(CO)_3$; (b) $Et_5C_5Mn(CO)_3$; (c) $C_5H_5Mn(CO)_2P(OPh)_3$; (d) $C_5H_5Mn(CO)_2$ $P(C_6H_{11})_3$. The observed CO stretching bands in the absence of $SnCl_4$ are shown dotted.

quantity of $SnCl_4$ added. Thus compounds 3–9 (Table 1) in the presence of a 2–4-fold excess of $SnCl_4$ exhibit only the new bands described above but no bands due to the starting compounds (Fig. 1). Compound 2 in which the electron-donor effect of P(OPh)$_3$ is considerably weaker relative to that of the $PPh_3$ ligand[5] exhibits both doublets even with a 5–8-fold excess of $SnCl_4$. The parent compound in this series, namely CpMn(CO)$_3$, does not react with $SnCl_4$ as demonstrated by the fact that its solution remained the same colour and that its spectrum contained only bands attributable to the starting compounds. The ratio of optical densities of the absorption bands was not measured because of the inhomogeneity of the system. The relative basicity of compounds 2–9 towards adduct formation with $SnCl_4$ may be described in terms of the equilibrium constant for the process but again due to the inhomogeneity of the system it was not possible to obtain reproducible results.

The results obtained may be explained by assuming that a reversible equilibrium is set up between the starting compounds and adducts (II) formed in $CH_2Cl_2$ solution:

$$\underset{\text{(I)}}{CpMn(CO)_2L + nSnCl_4} \rightleftarrows \underset{\text{(II)}}{CpMn(CO)_2L \cdot nSnCl_4}$$

That such an equilibrium exists is supported by the following facts:

(*i*) The ratio of band intensities for compounds (I) and (II) depends on the amount of $SnCl_4$ added, the equilibrium shifting to the right when excess $SnCl_4$ is present.

(*ii*) Addition of solvent shifts the equilibrium to the left-hand side thus indicating the reversibility of the process.

(*iii*) Treatment of the reaction mixture with water results in the formation of the starting compound (I).

The change in character of the IR spectra in the presence of $SnCl_4$ and the observed $\nu$(CO) shifts are similar to those observed earlier during protonation of the same compounds in acidic media[3]. The equilibrium position attained during the reaction of (I) with $SnCl_4$ is determined by the change in the basicity of the manganese atom. The latter depends on the nature of the ligand L and on the position and character of the substituents in the Cp ligand. In the series of compounds 1–9, the basicity of the Mn atom increases as the electron donor ability of L increases, and this leads to a shift of the equilibrium towards the adduct (II). The compound $CpMn(CO)_3$ does not react with $SnCl_4$, but compound 10, in which all five hydrogen atoms in the Cp ligand are substituted by donor groups (ethyl), forms an adduct with $SnCl_4$ although in this case the equilibrium is shifted markedly to the left-hand side.

Formation of an adduct with $SnCl_4$ results in a decrease in the electron density at Mn which decreases the $d_\pi$(Mn)–$p_\pi$(CO) back-donation and increases the frequency of $\nu$(CO). Compounds of type (I) do not react with weaker aprotic acids such as $HgCl_2$ and $GeCl_4$ even when these are present in large excess. In the presence of a large excess of $SbCl_3$ the resulting solution exhibits new bands shifted to greater frequencies, but of negligible intensity, *i.e.* the equilibrium is shifted almost completely towards the starting compounds. In the presence of excess $SbCl_5$ the starting compounds decomposed. Equimolar amounts of compounds 1 and 3 did not react with $SbCl_5$, whereas with compound 9 approximately equal quantities of the starting materials and the product were present in the solution.

In most cases where the structures of the adducts formed between transition metal complexes and Lewis acids are described in the literature it is assumed that the Lewis acid reacts directly with the transition metal atom[4,6]. This fact, together with the similarity between our present results and the protonation data[1-3], suggests that the same kind of bonding is present here.

It is interesting to note that a more complicated type of IR spectrum was obtained when compounds 3, 4 and 6–9 were treated with $SnCl_4$. Each new band formed was further split into two bands separated by 10–15 $cm^{-1}$ (*cf.* Fig. 1d), the relative intensity of each component in the doublet depending on the reagent ratio employed and the concentration. This may be attributed either to the presence of complexes with different geometry (*i.e. cis* or *trans* location of the Sn atom with respect to the phosphine ligand) or to the formation of complexes of different composition. The latter supposition is confirmed by the analytical data for the solid 1/2 adduct obtained from the reaction solution between $CpMn(CO)_2PPh_3$ and $SnCl_4$. The data on the composition and structure of the adducts prepared will be published in a separate paper.

Substitution of two CO groups in $CpMn(CO)_3$ by two phosphine ligands results in an even greater basicity for the manganese atom relative to the mono-substituted species. Diphosphine complexes of the type $CpMn(CO)L_2$ (III) [where $L_2=(PPh_3)_2$ or bidentate chelate ditertiary phosphine, *viz.* $Ph_2P(CH_2)_nPPh_2$ ($n=1$–3)] react not only with $SnCl_4$ but also with weaker aprotic acids such as $SbCl_3$, $HgCl_2$ and $GeCl_4$ (Table 2). In each case a single $\nu$(CO) frequency is enhanced by 100–110 $cm^{-1}$, the bands of both forms or of the adducts (IV) alone appearing in the spectrum depending on the ratio of starting reagents:

$$\underset{\text{(III)}}{CpMn(CO)L_2}+n\,Y \rightleftarrows \underset{\text{(IV)}}{CpMn(CO)L_2\cdot nY}$$

$$Y = SnCl_4, SbCl_3, HgCl_2 \text{ or } GeCl_4$$

In the presence of excess $SnCl_4$, $SbCl_3$ or $HgCl_2$ bands corresponding to the starting compounds were absent and the IR spectrum of the solution contained only those of the adduct. With $GeCl_4$, even present in large excess, the IR spectrum of the solution exhibited both bands, their intensity ratio indicating a shift of the equilibrium towards the starting compounds.

Hence cyclopentadienylphosphine complexes of manganese react with Lewis acids in $CH_2Cl_2$ solution at room temperature. Adduct formation in the solution is reversible, the position of the equilibrium depending upon the nature of the ligand L, the presence of substituents in the Cp ligand and on the strength of the Lewis acid. The data obtained indicate that the following series applies regarding the relative abilities of the Lewis acids investigated towards adduct formation: $SnCl_4 > SbCl_3 > HgCl_2 > GeCl_4$.

## EXPERIMENTAL

The IR spectra were measured using a Zeiss UR-20 spectrometer with an LiF prism. The instrument was calibrated using the DCl vibration–rotation spectrum. The compounds $CpMn(CO)_2L$ and $CpMn(CO)L_2$ were prepared as described earlier[3,7,8]. Before being employed in the measurements, $CH_2Cl_2$ was dried and distilled over $P_2O_5$. The measurements were made using cells of 0.1 mm thickness.

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