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# STERIC EFFECTS OF PHOSPHINE LIGANDS ON THE PHOTOCHEMISTRY OF $Mn_2(CO)_{10}$

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## Summary

The photochemistry of $Mn_2(CO)_{10}$ in the presence of phosphine ligands has been investigated. Steric hindrance by the phosphine molecules influences the products of the photolysis reaction. With ethyldiphenylphosphine disubstituted symmetrical species are obtained.

## Introduction

The photochemistry of $Mn_2(CO)_{10}$ has been extensively investigated [1]. Much attention has been given to the primary photoprocess:

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2\ {\cdot}Mn(CO)_5$$

but some uncertainty still remains about the final products of the reaction, especially when donor ligands are present. In previous work [2] we observed that in the presence of nitrogen donor ligands the following disproportionation reaction takes place:

$$Mn_2(CO)_{10} \xrightarrow[L]{h\nu} Mn^{2+} + Mn(CO)_4L^-$$

(L = ligand)

In this reaction only one L molecule can enter the coordination sphere of manganese.

More recent studies [3] have shown that phosphine ligands can direct the photoreaction towards various pathways viz. (a) CO substitution, (b) hydrogen abstraction, and (c) disproportionation, depending on the steric hindrance of the phosphine. As the aim of our studies is the production of manganese(0) species bound to solid supports as potential catalysts, it seemed of interest to reexamine the photochemistry of $Mn_2(CO)_{10}$ in the presence of various phosphines, in order to provide more information on the influence of the steric hindrance on the products.

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## Experimental

ESR spectra were recorded on an E-line Varian spectrometer with a 12 inches magnet operating in the X band. The recording temperature was controlled by the use of the thermostat accessory. IR spectra were recorded on a Perkin–Elmer 612 spectrophotometer. $Mn_2(CO)_{10}$ was purchased from Fluka and sublimed before use. The $P(n\text{-}Bu)_3$, $PEtPh_2$ and $P(t\text{-}Bu)_3$ were purchased from Fluka and distilled before use.

Photolyses were performed under anhydrous nitrogen in a double-window quartz reactor provided with a cooling jacket. A high-pressure Hg lamp fitted with a cutoff UV35 filter was used as the light source.

Solutions of concentration up to $5 \times 10^{-3}$ *M* were prepared by degassing the solvent by freezing and subsequent distillation from previously sublimed manganese decacarbonyl. Phosphines were added to the $Mn_2(CO)_{10}$ solution in a 1/6 ratio with respect to the solvent by distillation following careful degassing.

## Results and discussion

The experiments were performed with three phosphines providing three different steric effects. Tri-n-butylphosphine has a cone angle [4] of 132°, ethyldiphenylphos-

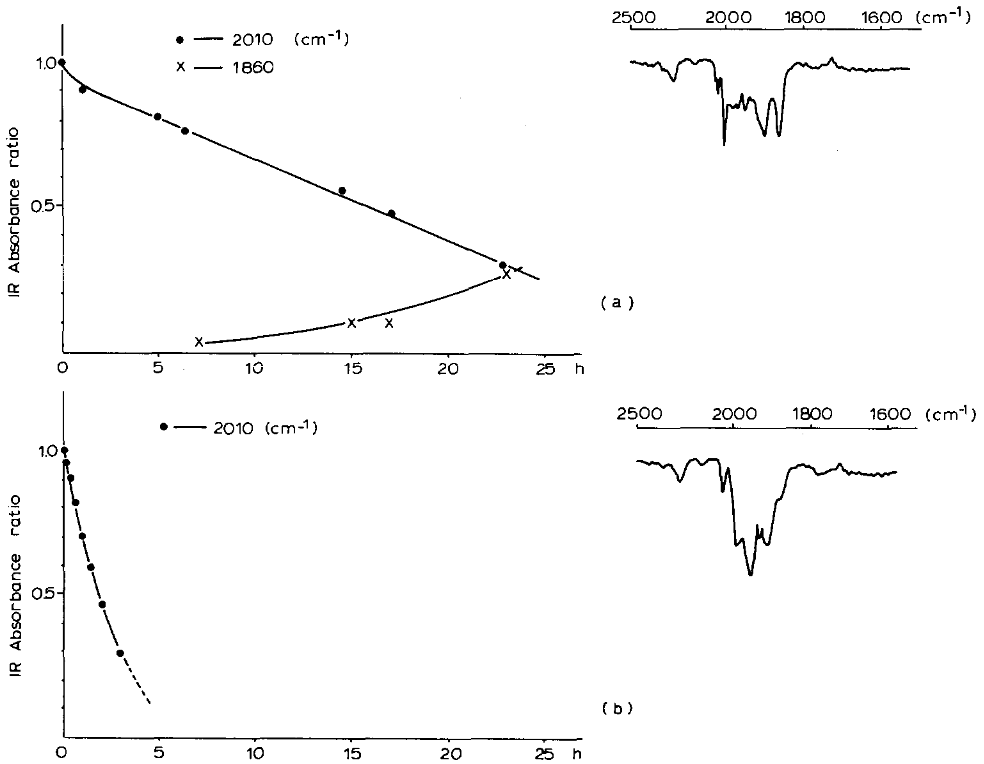

Fig. 1. Photochemistry of $Mn_2(CO)_{10}$ with tri-t-butylphosphine (a): *T* 250 K; (b): *T* 297 K. (IR absorbance ratios were calculated with the $Mn_2(CO)_{10}$ absorbance as reference.)

phine 140° and tri-t-butylphosphine 180°, respectively.

Kinetic features of the photoreaction in the presence of tri-t-butylphosphine at two temperatures and the corresponding final IR spectra are reported in Fig. 1. As can be seen, at 250 K (Fig. 1a) the slow disappearance of $Mn_2(CO)_{10}$ (IR maximum at 2010 $cm^{-1}$) is accompanied by the formation of $\cdot Mn(CO)_5$ (IR maximum at 1860 $cm^{-1}$ [5] in accord with disproportionation [6]. The ESR spectrum (Fig. 2) confirms the growth of the cation $Mn^{2+}$ ($a$(Mn) 9.1 mT [7]). At 297 K (Fig. 1b) the rate of disappearance of $Mn_2(CO)_{10}$ is increased and the IR spectrum shows a multiple absorption in the range 1900–2000 $cm^{-1}$ with a maximum at 1990 $cm^{-1}$. These absorptions probably belong to variously substituted species among which the monosubstituted dimer $Mn_2(CO)_9P(R)_3$ predominates. In the presence of ethyldiphenylphosphine (Fig. 3), at 250 K $R_3P(CO)_4Mn{-}Mn(CO)_4PR_3$ appears to be the only product of the photoreaction (IR maximum at 1950 $cm^{-1}$ [8,3b]): its concentration reaches a maximum and then slowly decreases (graphic 3a); the corresponding ESR spectrum, however, (Fig. 4) shows in addition the formation of the paramagnetic disubstituted species $\cdot Mn(CO)_3(PR_3)_2$ [3c]. On increasing the temperature (Fig. 3b) the stability of the symmetric disubstituted dimer decreases, while the paramagnetic species is converted into the hydride $HMn(CO)_3(PR_3)_2$(IR maximum at 1890 $cm^{-1}$ [3b]) and, to a lesser extent, into disproportionation products, as indicated by the ESR spectrum for $Mn^{2+}$ and by the IR maxima at 1860 $cm^{-1}$ for $\cdot Mn(CO)_5$ and 1780 $cm^{-1}$ for $\cdot Mn(CO)_4PR_3$ [5b]. On further decrease in the cone angle, with tri-n-butylphosphine a general rate increase of the reactions described for the ethyldiphenyl derivative can be observed at both temperatures (Fig. 5). The same reaction was also carried out in a CO atmosphere at 250 K; a slight decrease of the rates, possibly as a consequence of a more difficult substitution reaction, seems to be the only effect (Fig. 5c).

Our results can be rationalized on the basis of the mechanism formulated by Brown [3,9]:

(a) $Mn_2(CO)_{10} \rightarrow 2\cdot Mn(CO)_5 \rightarrow$ disproportionation products

(b) $\cdot Mn(CO)_5 + L \rightarrow \cdot Mn(CO)_4L + CO$

(c) $\cdot Mn(CO)_5 + \cdot Mn(CO)_4L \rightarrow Mn_2(CO)_9L$

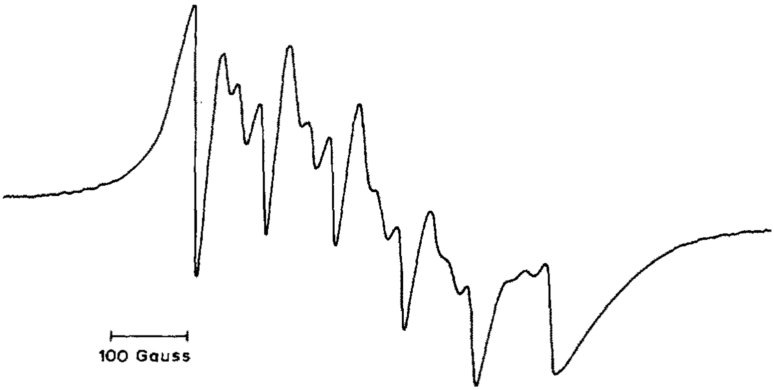

Fig. 2. ESR final spectrum of the solution of Fig. 1a (recorded at liquid $N_2$ temperature).

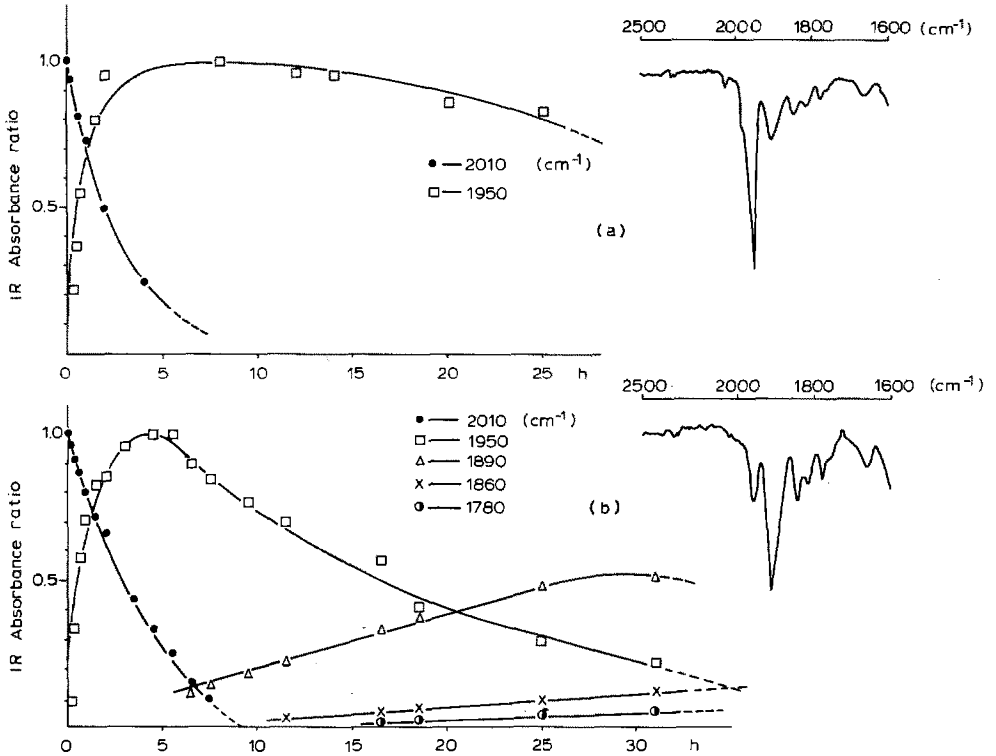

Fig. 3. Photochemistry of $Mn_2(CO)_{10}$ with ethyldiphenylphosphine (a): $T$ 250 K; (b): $T$ 297 K. (IR absorbance ratios were calculated with the $Mn_2(CO)_{10}$ absorbance as reference.)

(d) $\cdot Mn(CO)_4L + L \rightarrow \cdot Mn(CO)_3L_2 + CO$
(e) $\cdot Mn(CO)_4L + \cdot Mn(CO)_4L \rightarrow Mn_2(CO)_8L_2$
(f) $\cdot Mn(CO)_4L + \cdot Mn(CO)_3L_2 \rightarrow Mn_2(CO)_7L_3$
(g) $\cdot Mn(CO)_3L_2 + HR \rightarrow HMn(CO)_3L_2 + R\cdot$

The steric hindrance of the phosphine plays a key role in the extent of substitution of CO molecules with the donor ligand in the primary photolysis product $\cdot Mn(CO)_5$. In turn, depending on the extent of substitution, the paramagnetic species disappear by different routes: $\cdot Mn(CO)_5$ either recombines or disproportionates, $\cdot Mn(CO)_4P(R)_3$ is mainly converted into the disubstituted symmetric dimer, and $\cdot Mn(CO)_3(PR_3)_2$ into the corresponding hydride $HMn(CO)_3(PR_3)_2$. In our system, with the bulky tri-t-butylphosphine at room temperature only monosubstitution occurs as indicated by the formation of $Mn_2(CO)_9PR_3$, while at 250 K the disproportionation products from $\cdot Mn(CO)_5$ are obtained. With ethyldiphenylphosphine both mono- and disubstitution become operative: $\cdot Mn(CO)_4PR_3$ forms the corresponding dimer, $\cdot Mn(CO)_3(PR_3)_2$, which is rather stable at 250 K but at room temperature abstracts hydrogen from the medium to give the hydride. Finally with tri-n-butylphosphine the disubstitution reaction predominates independent of the temperature, and the hydride is obtained as main product.

While the absence of recombination reaction for $\cdot Mn(CO)_3(PR_3)_2$ can be rationalized in terms of steric hindrance due to the presence of two phosphine

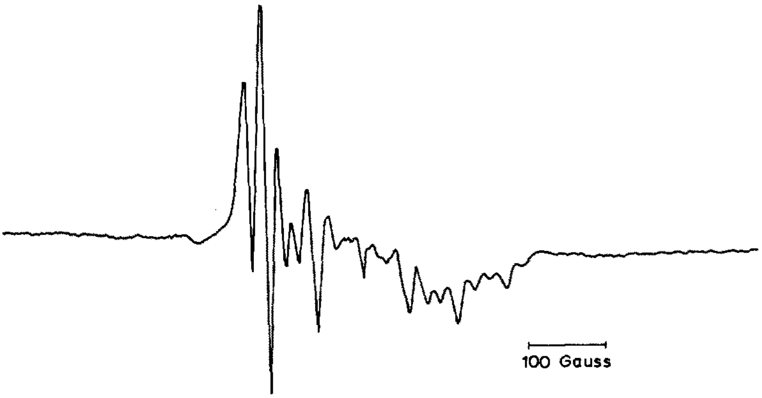

Fig. 4. ESR final spectrum of the solution of Fig. 3a (recorded at liquid $N_2$ temperature).

molecules on the same metallic center [3], it is more difficult to explain why hydrides such as $HMn(CO)_5$ and $HMn(CO)_4PR_3$ are not obtained. From our results it might be inferred that the strength of the metal–hydrogen bond is changed as one or more phosphines enter the coordination sphere of the metal, thus modifying the ligand field effect around the manganese nucleous.

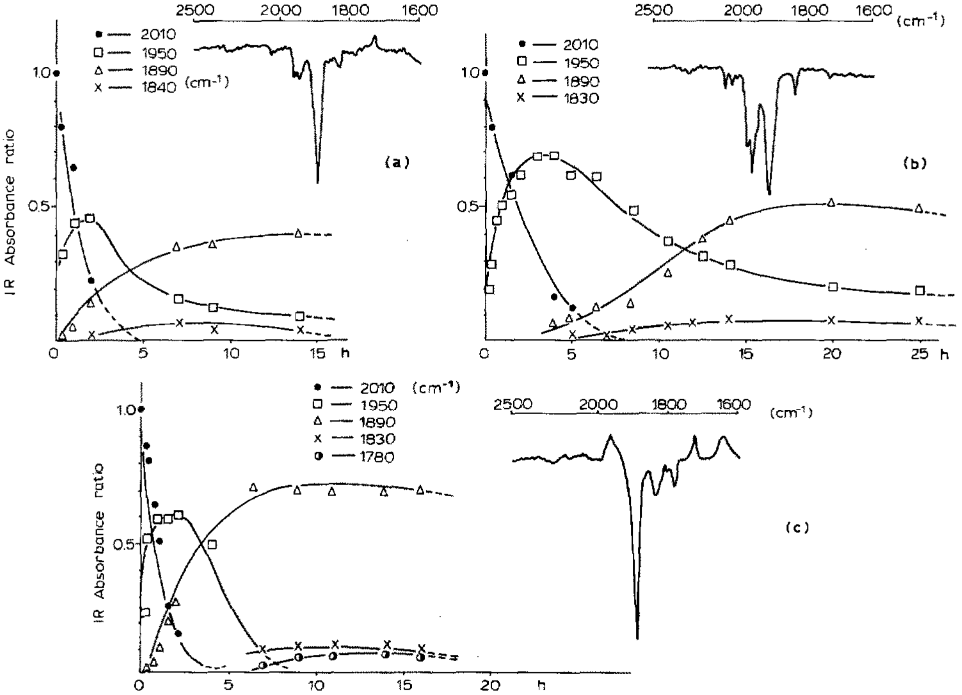

Fig. 5. Photochemistry of $Mn_2(CO)_{10}$ with tri-n-butylphosphine (a): $T$ 250 K under $N_2$; (b): $T$ 250 K under CO; (c): $T$ 297 K under $N_2$. (IR absorbance ratios were calculated with the $Mn_2(CO)_{10}$ absorbance as reference.)

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