Journal of Organometallic Chemistry, 84 (1975) 339—345

AN INVESTIGATION INTO THE MECHANISM OF CONVERSION OF *fac*-[$Mn(CO)_3\{P(OMe)_2Ph\}_2X$] ($X$ = Cl, Br) INTO *mer-cis*-[$Mn(CO)_2\{P(OMe)_2Ph\}_3X$] IN THE PRESENCE OF $P(OMe)_2Ph$

D.J.A. DE WAAL*, R.H. REIMANN and E. SINGLETON

National Chemical Research Laboratory, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria (Republic of South Africa)

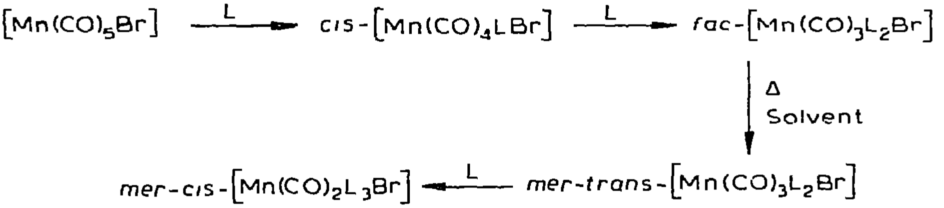
(Received July 15th, 1974)

Summary

The complex *mer-trans*-[$Mn(CO)_3\{P(OMe)_2Ph\}_2X$] ($X$ = Cl, Br) is an intermediate in the conversion of *fac*-[$Mn(CO)_3\{P(OMe)_2Ph\}_2X$] into *mer-cis*-[$Mn(CO)_2\{P(OMe)_2Ph\}_3X$] in the presence of $P(OMe)_2Ph$ in benzene. No direct route between the latter two complexes could be detected kinetically. The results imply a *trans* carbonyl disposition as a prerequisite for higher carbonyl substitution in octahedral Mn^I carbonyl complexes.

Introduction

From numerous [1-5] studies on the stepwise replacement of carbonyl ligands in [$Mn(CO)_5Br$] by phosphines, phosphites, phosphonites and arsines, a reaction scheme may be proposed (eqn. 1).



(1)

It was proposed from these investigations that the two controlling factors governing the substitution of carbonyl groups in [$Mn(CO)_5Br$] in particular and possibly in octahedral carbonyl complexes in general were: (*i*) carbonyl ligands

---

* Author to whom correspondence should be addressed.

trans to each other are preferentially replaced; (*ii*) the steric size of L is more important than its electronic properties [3,6].

Though limited supporting evidence for the *trans* CO groups requirement was obtained from ^{13}CO exchange work [7] on [$Mn(CO)_5Br$] and the formation of *fac*-[$Mn(CO)_3L_2X$] complexes from *cis*-[$Mn(CO)_4LX$] (in which in both cases the *trans* carbonyl groups are statistically favoured), no quantitative work has specifically shown that substitution only occurs with carbonyl groups in *trans* disposition to one another.

It was thus of interest to investigate kinetically the mechanistic pathway by which *fac*-[$Mn(CO)_3L_2X$] is converted into *mer-cis*-[$Mn(CO)_2L_3X$] on reacting with L, and hence to establish the carbonyl *trans* to carbonyl prerequisite for the substitution reactions in manganese carbonyl halides. For this investigation L was chosen as $P(OMe)_2Ph$ for reasons that will be outlined in the discussion.

Experimental

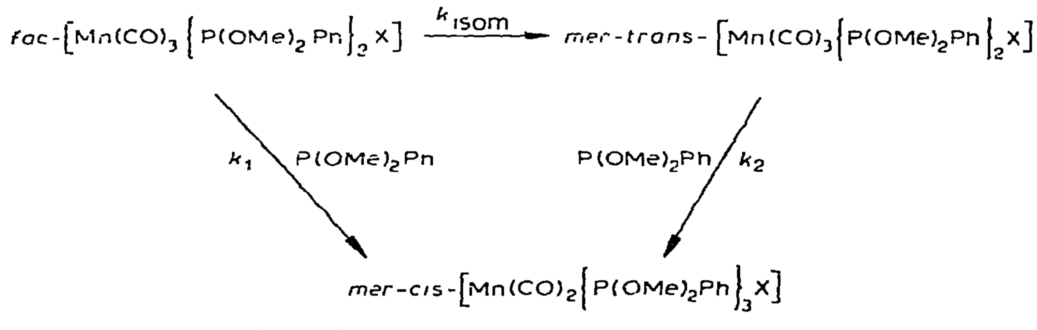
Spectroscopically pure benzene and dimethylformamide were purchased from Merck. The pure complexes *fac*-[$Mn(CO)_3\{P(OMe)_2Ph\}_2X$], the corresponding *mer-trans* isomer and *mer-cis*-[$Mn(CO)_2\{P(OMe)_2Ph\}_3X$] were prepared and characterised by established methods [3]. The extreme conditions required to prepare the corresponding iodo complexes rendered a mechanistic study of their reactions unattractive.

Rates of reaction were measured by following the change in optical density with a Cary-14 spectrophotometer equipped with a cell compartment thermostatted to ± 0.2°. The concentration of the substrate was approximately 10^{-3} *M* and that of the added $P(OMe)_2Ph$ ranged from 0.0-0.1 *M*. The reactions were initiated by dissolving a small amount of solid substrate in a thermostatted stoppered cell containing solvent and the appropriate amount of $P(OMe)_2Ph$.

Results and discussion

Possible reaction pathways are depicted in Scheme 1. The distinct UV spectra displayed by these three complexes are given in Fig. 1. In solution *fac*-[$Mn(CO)_3\{P(OMe)_2Ph\}_2X$] isomerises quantitatively to the *mer-trans* configuration and the reaction is characterised by two isosbestic points at 360 and 405 nm in the UV range of the absorption spectrum.

SCHEME 1



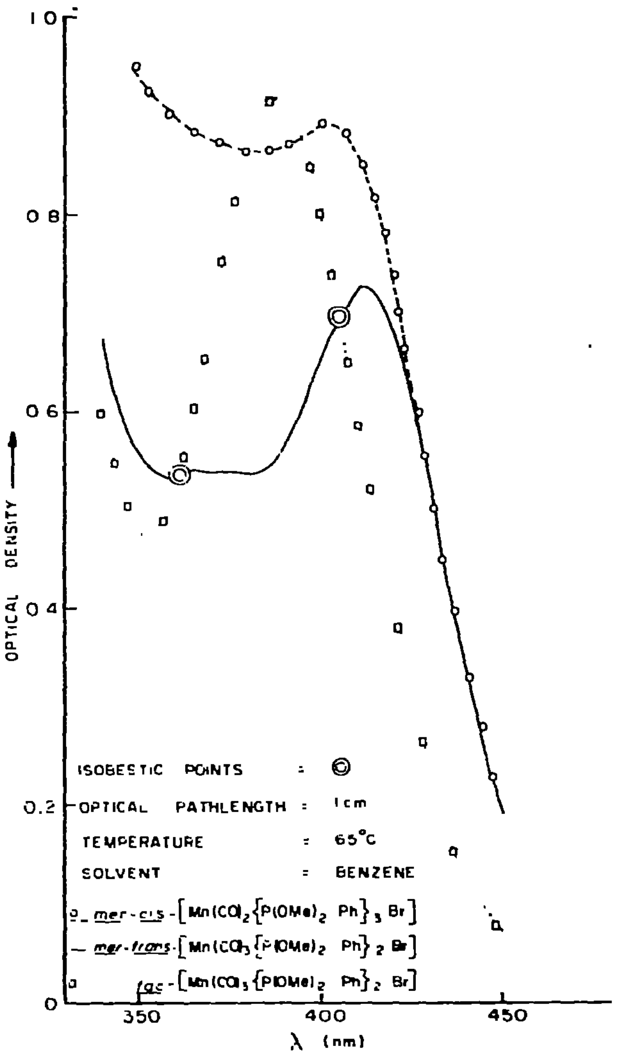


Fig. 1. The ligand field spectra of *fac*- and *mer-trans*-$[Mn(CO)_3\{P(OMe)_2Ph\}_2Br]$ and *mer-cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3Br]$.

Addition of free $P(OMe)_2Ph$ to a solution containing either the *fac* or the *mer-trans* disubstituted complexes produced *mer-cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3X]$. Attempts to measure the specific rate constant k_2 using *mer-trans*-$[Mn(CO)_3\{P(OMe)_2Ph\}_2X]$ as the substrate failed because a marked deviation from pseudo first-order was obtained. This was observed as a non-linear plot of log $(A_\infty - A_t)$ versus reaction time where A_t and A_∞ represent the UV absorption of the reaction at time t and at completion, respectively. Carbonylation studies [3] on *mer-cis*-$[Mn(CO)_2L_3Br]$ systems have shown the existence of the equilibrium:

mer-cis-$[Mn(CO)_2L_3Br]$ + CO $\rightleftharpoons$ *mer-trans*-$[Mn(CO)_3L_2Br]$ + L

and this seems the most likely explanation for the observed deviation from linearity of the plots. Because in this study the reaction of the disubstituted complex with $P(OMe)_2Ph$ to give the trisubstituted product will produce CO at a concentration not much greater than the concentration of *mer-cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3Br]$, a deviation from pseudo first-order kinetics can be expected as the contribution of the reverse carbonylation reaction to the overall rate of reaction becomes more prominent.

Kinetic data collected by monitoring optical density changes at the wavelength 425 nm gave excellent linear plots of log $(A_\infty - A_t)$ versus reaction time for more than 90% of the reaction. These data were reproducible to within 5% and are collected in Table 1. From Fig. 1 it can be seen that any contribution by the kinetic pathway k_2 is filtered out by a isosbestic point at 425 nm. Reactions k_1 and k_{isom} are therefore the only ones responsible for any optical density changes at this wavelength. With no $P(OMe)_2Ph$ added to the reaction solution, k_{obs} is equal to k_{isom}. Any significant contribution from k_1 can be ruled out because k_{obs} still equalled the numerical value of k_{isom} if various amounts of $P(OMe)_2Ph$ were added to the reaction solution. Furthermore the fortuitous case where $k_{\text{isom}} = k_1$ is invalidated because *fac*-$[Mn(CO)_3\{P(OMe)_2Ph\}_2X]$ does not react at twice the rate of isomerisation when $P(OMe)_2Ph$ is introduced to the reaction solution. It thus appears that the formation of *mer-cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_3X]$ from *fac*-$[Mn(CO)_3\{P(OMe)_2Ph\}_2X]$ is controlled by the rate of isomerisation of the latter complex to the *mer-trans* isomer and hence there

TABLE 1

FIRST-ORDER RATE CONSTANTS FOR THE ISOMERISATION OF *fac*-$[Mn(CO)_3\{P(OMe)_2Ph\}_2X]$

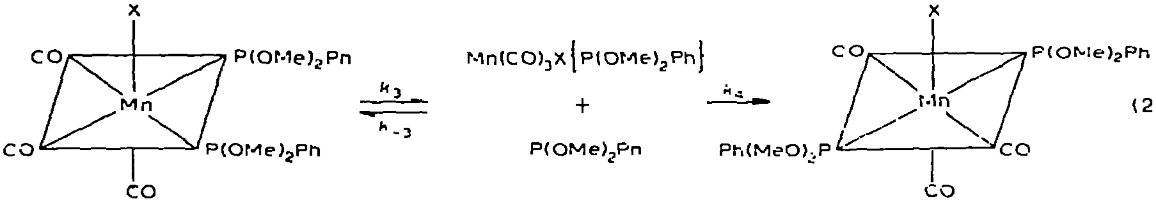
X	Temp. (°C)	$[P(OMe)_2Ph]$ (*M*)	Solvent	$k_{\text{obs}} \times 10^4 (s^{-1})$
Cl	41.0	0.0	C_6H_6	1.67
	41.0	0.01	C_6H_6	1.63
	41.0	0.05	C_6H_6	1.70
	41.0	0.1	C_6H_6	1.67
	41.0	0.0	DMF	1.04
	41.0	0.05	DMF	1.09
	41.0	0.10	DMF	1.06
	48.0	0.0	C_6H_6	4.4
	48.0	0.05	C_6H_6	4.25
	48.0	0.10	C_6H_6	4.5
	48.0	0.0	DMF	3.0
	48.0	0.05	DMF	3.1
	52.2	0.0	C_6H_6	8.70
	52.2	0.1	C_6H_6	8.50
	52.2	0.0	DMF	5.95
	52.2	0.05	DMF	5.70
Br	41.0	0.0	C_6H_6	0.358
	41.0	0.01	C_6H_6	0.365
	41.0	0.05	C_6H_6	0.370
	41.0	0.1	C_6H_6	0.365
	48.0	0.0	C_6H_6	1.06
	48.0	0.05	C_6H_6	1.08
	48.0	0.1	C_6H_6	1.04
	53.0	0.0	C_6H_6	2.4
	53.0	0.1	C_6H_6	2.2

[a] Substrate concentration ~10^{-3} *M*.

is no direct reaction path k_1 under the experimental conditions adopted for this investigation. The kinetic *trans* effect is well established for square planar systems [8] and studies on the substitution reactions of $\mathrm{Pt^{II}}$ complexes have shown that CO has a stronger *trans* labilising influence than tertiary phosphine ligands [8]. A similar trend is observed here for octahedral $\mathrm{Mn^I}$ carbonyl complexes.

Attempts to extend this study to corresponding complexes with L = $P(OMe)_3$, PMe_3, $P(OEt)_3$ or PMe_2Ph failed because no isosbestic point in the UV absorption spectra of these *mer-trans* tricarbonyl and the *mer-cis* dicarbonyl complexes could be detected. The complications caused by the reversible carbonylation reaction could therefore not be circumvented.

The mechanism for the *fac* → *mer-trans* isomerisation is most probably S_N1 involving a five coordinated intermediate formed by dissociation of a phosphonite ligand (eqn. 2). A carbonyl dissociation from the *fac*-isomer is ruled out since the isomerisation also went to completion if the reaction solution was flushed with an inert gas such as nitrogen.



(2)

The positive values found for ΔS^* (Table 2) are in agreement with a reaction in which the major activation process is dissociative in nature [2]. The rate of isomerisation is not significantly influenced by the dielectric properties of the solvent as disclosed by the data in Table 2, which supports the non-ionic nature of the activation process of the proposed mechanism.

From the proposed reaction 2 a theoretical rate law can be derived (eqn. 3)

$$k_{\mathrm{obs}} = \frac{k_3 \cdot k_4\,[\mathrm{P(OMe)_2Ph}]}{k_4\,[\mathrm{P(OMe)_2Ph}] + k_{-3}\,[\mathrm{P(OMe)_2Ph}]} = \frac{k_3 \cdot k_4}{k_4 + k_{-3}} \qquad (3)$$

Two limiting cases can be applied to eqn. 3 (eqns. 4 and 5).

$$k_{\mathrm{obs}} = k_3 \text{ if } k_4 \gg k_{-3} \qquad (4)$$

$$k_{\mathrm{obs}} = k_3 \cdot k_4/k_{-3} \text{ if } k_4 \ll k_{-3} \qquad (5)$$

An important prerequisite for the validity of the proposed mechanism that emerges from the theoretical rate laws 3, 4 or 5, is that the addition of $P(OMe)_2Ph$ to the reaction solution should have no influence on the rate of isomerisation, as was found to be the case (Table 1). The kinetic results listed in Table 1 can be accommodated by the experimental rate law described in eqn. 6.

$$k_{\mathrm{obs}} = \text{Constant} \qquad (6)$$

Equation 6 thus tallies with either of the theoretical rate laws 3, 4 or 5. We give preference to the rate law 3 as a true representation of the experimental facts, because the possibility that the rate constants k_{-3} and k_4 differ significantly, as

TABLE 2

ACTIVATION PARAMETERS FOR THE ISOMERISATION OF *fac*-$MnX(CO)_3\{P(OMe)_2Ph\}_2$ IN DIFFERENT SOLVENTS

X	$k_{obs} \times 10^6$ [a] (s^{-1})	E_a (kcal mol^{-1})	ΔS^* (cal mol^{-1} K^{-1})	Solvent	Dielectric constant
Cl	12.6	30.0 ± 0.5	17.7	C_6H_6	2.0[b]
Cl	8.0	30.6 ± 0.5	18.7	DMF	36.7[c]
Br	2.5	31.3 ± 0.2	18.8	C_6H_6	2.0[b]

[a] k_{obs} calculated from the Arrhenius plots extrapolated to 25°. [b] Ref. 16. [c] Ref. 17.

implied by eqs. 4 or 5, is highly unlikely since both kinetic pathways incorporate the same reactants.

In sharp contrast to our results previous workers have found the isomerisation of *fac*-$[Mn(CO)_3\{P(OPh)_3\}_2Br]$ to be suppressed by free phosphite in solution [5]. This type of behaviour suggests an association between the substrate and $P(OPh)_3$ in the activated complex which is rather unusual for typical octahedral substitution reactions. The lack of charge on the reactants as well as the independence of the rate of reaction on the polarity of the solvent renders the I_d-interchange mechanism improbable [9,10].

A marked decrease in the rate of CO dissociation from the complexes $[Mn(CO)_5X]$ [4,11] and *fac*-$[Mn(CO)_4LX]$ [12] on varying the halogen from Cl to I has previously been explained by stronger metal to carbonyl π-bonding as the electron density on the metal atom increased. The reactivity order was established as I/Br/Cl 1/8/200. By making use of this postulate Spendjian and Butler [13] concluded that no significant π-back bonding between Mn^I and tertiary phosphines occurs since the dissociation of PPh_3 from *mer-trans*-$[Mn(CO)_3(PPh_3)_2X]$ was not influenced by changing the halogen X. However, from the trend in the rate constants (Table 2) of the present investigation, it appears that some degree of Mn^I—phosphonite π-back bonding is indicated which is in agreement with the accepted π-acceptor order [14]: CO $\gg$ phosphite > phosphine.

The *fac* → *mer-trans* isomerisations of $[Mn(CO)_3L_2X]$ occur in either polar or non-polar solvents and this fact together with reported work [4,5,15] provides further evidence that steric interaction of the *cis* ligands is the driving force in these isomerisations. In addition to steric properties, however, electronic factors do play an influential role as revealed by the reactivity order Cl > Br reported above.

References

1 T.A. Manuel, Advan. Organometal. Chem., 3 (1965) 181.
2 R.J. Angelici, Organometal. Chem. Rev., 3 (1968) 173.
3 R.H. Reimann and E. Singleton, J. Chem. Soc., Dalton, (1973) 841.
4 R.J. Angelici and F. Basolo, J. Amer. Chem. Soc., 84 (1962) 2495.
5 R.J. Angelici, F. Basolo and A. Poë, J. Amer. Chem. Soc., 85 (1963) 2215.
6 R.H. Reimann and E. Singleton, J. Organometal. Chem., 44 (1972) C18.
7 A. Berry and T.L. Brown, Inorg. Chem., 11 (1972) 1165.
8 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, Second Edition, Wiley, New York, 1965, p. 351.

9 C.H. Langford and H.B. Gray, Ligand Substitution Processes, W.A. Benjamin, Inc., New York, 1965 p. 8 and 84.
10 Ref. 8, p. 197.
11 A. Wojcicki and F. Basolo, J. Amer. Chem. Soc., 83 (1961) 525.
12 R.J. Angelici and F. Basolo, Inorg. Chem., 2 (1963) 728.
13 H.K. Spendjian and I.S. Butler, Inorg. Chem., 9 (1970) 1268.
14 W.A.G. Graham, Inorg. Chem., 7 (1968) 315.
15 E.W. Abel and G. Wilkinson, J. Chem. Soc. (1959) 1501.
16 Handbook of Chemistry and Physics, The Chemical Rubber Company, 53rd edn., 1972-1973.
17 H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolytic Solutions, Reinhold Publishing Corp., New York, 1943.