The Co-ordination of Small Molecules by Manganese(II) Phosphine Complexes. Part 9.[1] The Reaction of Ethylene with $[MnX_2L]$ (X = Cl, Br, or I; L = PPr^n_3, PBu^n_3, $PPhMe_2$, $PPhEt_2$, or PPh_3) in Tetrahydrofuran Solution†

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The reaction of the $[MnX_2L]$ complexes (X = Cl, Br, or I; L = PPr^n_3, PBu^n_3, $PPhMe_2$, $PPhEt_2$, or PPh_3) with ethylene has been studied in tetrahydrofuran solution. The complexes with X = Cl, L = PPr^n_3, PBu^n_3, $PPhMe_2$, or $PPhEt_2$ and X = Br, L = PBu^n_3 were found to react in a 1 : 1 ratio, whereas the other complexes were found to be inactive towards ethylene. This order of binding ability, *i.e.* Cl > Br ≫ I, contrasts markedly with the ability of the $[MnX_2L]$ complexes to bind sulphur dioxide, for which the order is I > Br ≫ Cl.

Because of the large 'blank' solvent absorption of ethylene, there are few if any studies on the uptake of ethylene by metal complexes in solution in organic solvents, although there have been numerous studies on the uptake of ethylene and other gaseous alkenes by aqueous solutions of silver(I) salts.[2]

The reaction of the $[MnX_2L]$ (L = tertiary phosphine) complexes with dioxygen,[3] carbon monoxide,[4] and nitric oxide[5] have been extensively studied in both the solid state and in solution. The reactions of gases such as carbon dioxide and ethylene have also been studied[6] but, because of their high solubility in organic solvents, the investigations have previously been confined to the solid state. However, a method for studying the uptake of sulphur dioxide, which is also extremely soluble in organic solvents, by the $[MnX_2L]$ complexes has recently been developed,[7] and so it has now been possible to study the uptake of ethylene by these complexes in solution. The method involves the use of an ethylene–argon mixture, thereby reducing the volume of gas absorbed by the solvent alone, and thus making it possible to study the uptake of ethylene by solutions of the concentrations attainable for the $[MnX_2L]$ complexes. We have recently reported the isolation of 1 : 1 adducts, $[MnX_2L(tcne)]$, formed between the manganese(II) phosphine complexes and tetracyanoethylene (tcne).[8]

Results and Discussion

The apparatus and method employed for the study of ethylene uptake by tetrahydrofuran (thf) solutions of $[MnX_2L]$ complexes has been described fully.[2,7] Briefly, a known pressure of ethylene was admitted to the system, which consisted of a mixing bulb (3 l) and a gas burette, and then the whole system was brought to atmospheric pressure (1 atm) with argon. The gas mixture was left for 2 h to allow thorough mixing and then the system was connected to the flask containing the solution under investigation and the gas uptake performed.

First, it was necessary to perform a series of 'blank' uptakes of gas mixtures, containing different concentrations of ethylene, by thf (50 cm^3) alone at 0 °C. The results are given in Table 1. Analysis of these results to obtain the final partial pressure of ethylene in the gas mixture (*i.e.* at the end of the uptake) and the volume of ethylene absorbed by the thf was made using equations (1) and (2), where P = atmospheric pressure, x_{Ar},

$$P_{C_2H_4} = P\{1 - [(x_{Ar}V')/(V + V^{\circ\prime} - V)]\} \quad (1)$$

$$V_{C_2H_4} = x_{C_2H_4}V' - V + [(x_{Ar}VV')/(V + V^{\circ\prime} - V^{\circ})] \quad (2)$$

$x_{C_2H_4}$ = mole fraction of argon or ethylene in initial mixture, V' = initial volume of mixture, V = final volume of mixture = V' − volume of gas absorbed ($\bar{V}$), $V^{\circ\prime}$ = initial volume of argon when $P_{C_2H_4} = 0$, and V° = final volume of argon when $P_{C_2H_4} = 0$. From Table 1 it can be seen that $V^{\circ\prime} - V^{\circ} = 2.9$ cm^3.

The derivation of these equations is given fully elsewhere.‡ The final partial pressure of ethylene and the volume of ethylene absorbed by the thf are given in Table 1. It can be seen that ethylene does not obey Henry's law. However, this is not a necessary condition for equations (1) and (2) to be valid (see ref. 7), although it must be assumed that argon does obey Henry's law, which is not unreasonable since argon is a noble gas.

A 'working' ethylene partial pressure of 120 mmHg was chosen for the uptakes by the solutions investigated. Gas uptakes were performed on aliquots (50 cm^3) of thf solutions of the $[MnX_2L]$ complexes (X = Cl, Br, or I; L = PPr^n_3, PBu^n_3, $PPhMe_2$, $PPhEt_2$, or PPh_3) at 0 °C. The results of the uptakes are shown in Table 2. It can be seen that as for other small molecules (*e.g.* dioxygen and carbon monoxide) all three of the PPh_3 complexes are inactive towards ethylene. For the other complexes, all of the chlorides reacted with ethylene in a 1 : 1 ratio (within experimental error) whilst none of the iodides reacted. In the case of the bromides, only $[MnBr_2(PBu^n_3)]$ was found to react, and again the reaction was in a 1 : 1 ratio. The complexes appear reversibly to bind ethylene, desorption being effected by warming the solution under a static vacuum. This was shown quantitatively for $[MnCl_2(PPhEt_2)]$. Once an uptake had been performed at 0 °C the solution was warmed to 30 °C under a static vacuum. The uptake was then repeated. As can be seen from Table 3, reversibility of binding is essentially demonstrated by the three cycles.

We have also studied uptakes by solutions of the complexes cooled in solid CO_2 to see if reaction with ethylene would occur at lower temperatures. At *ca.* −65 °C the thf (50 cm^3) blank absorption was found to be 33.0 ± 0.4 cm^3 of a gas mixture with an ethylene partial pressure of 120 mmHg. Because of the large blank uptake and the low solubilities of the chloride and bromide complexes at this temperature, only solutions of the iodide complexes were studied. The results of the uptakes, Table 4, show that the total gas absorption is equivalent to that of the thf solvent alone. Thus, the iodide complexes do not absorb ethylene either at 0 or at *ca.* −65 °C.

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† *Non-S.I. units employed:* atm = 101 325 N m^{-2}, mmHg ≈ 133 Pa.

‡ Derivation by Dr. J. Lee deposited as Supplementary Publication No. SUP 56350 of ref. 7.

Table 1. Analysis of uptakes by 50 cm^3 of thf at 0 °C

Initial partial pressure of ethylene/mmHg	x_{Ar}	V'/cm^3	Volume of gas mixture absorbed V/cm^3	Final partial pressure of ethylene/mmHg	Volume of ethylene absorbed/cm^3
0	1	3 640.8	2.9	0	0
30	0.96	3 630.2	4.7	30	1.9
60	0.92	3 625.6	7.2	60	4.5
90	0.88	3 630.1	10.7	90	8.1
120	0.84	3 632.2	14.0	119.6	11.6

Table 2. Uptake data for tetrahydrofuran solutions of the $[MnX_2L]$ complexes

Complex	Concentration/ mol dm^{-3}	V'/cm^3	$\bar{V}$/cm^3	$P_{C_2H_4}$/mmHg	Volume of ethylene absorbed/cm^3			Mn:C$_2$H$_4$ [b]
					By solution	By solvent [a]	By complex	
$[MnCl_2(PPr^n_3)]$	3.6×10^{-3}	3 632.0	17.8	119.0	15.4	11.5	3.9	1.03
$[MnBr_2(PPr^n_3)]$	4.6×10^{-3}	3 633.4	13.8	119.7	11.4	11.6	0	
$[MnI_2(PPr^n_3)]$	8.8×10^{-3}	3 626.8	13.8	119.7	11.4	11.6	0	
$[MnCl_2(PBu^n_3)]$	3.8×10^{-3}	3 636.5	18.1	118.9	15.7	11.5	4.2	1.01
$[MnBr_2(PBu^n_3)]$	5.5×10^{-3}	3 635.2	20.4	118.5	18.0	11.45	6.55	0.94
$[MnI_2(PBu^n_3)]$	1.69×10^{-3}	3 628.2	13.8	119.7	11.4	11.6	0	
$[MnCl_2(PPhMe_2)]$	2.8×10^{-3}	3 633.0	17.0	119.1	14.6	11.5	3.1	1.01
$[MnBr_2(PPhMe_2)]$	6.5×10^{-3}	3 631.8	14.0	119.6	11.6	11.6	0	
$[MnI_2(PPhMe_2)]$	1.47×10^{-2}	3 632.1	13.9	119.7	11.5	11.6	0	
$[MnCl_2(PPhEt_2)]$	3.9×10^{-3}	3 624.8	17.8	119.0	15.4	11.5	3.9	1.12
$[MnBr_2(PPhEt_2)]$	5.4×10^{-3}	3 624.4	15.2	119.4	12.8	11.6	0	
$[MnI_2(PPhEt_2)]$	1.73×10^{-2}	3 635.1	13.7	119.7	11.3	11.6	0	
$[MnCl_2(PPh_3)]$	2.6×10^{-3}	3 634.7	14.1	119.6	11.7	11.6	0	
$[MnBr_2(PPh_3)]$	3.4×10^{-3}	3 644.8	13.6	119.7	11.2	11.6	0	
$[MnI_2(PPh_3)]$	7.9×10^{-3}	3 624.8	13.9	119.7	11.5	11.6	0	

[a] From a plot of $V_{C_2H_4}$ *vs.* $P_{C_2H_4}$ for 'blank' uptakes. [b] Estimated error is ±0.1.

Table 3. Repeated uptakes from a 3.9×10^{-3} mol dm^{-3} tetrahydrofuran solution of $[MnCl_2(PPhEt_2)]$

Cycle	V'/cm^3	$\bar{V}$/cm^3	$P_{C_2H_4}$/mmHg	Volume of ethylene absorbed/cm^3		
				By solution	By solvent	By complex
1	3 624.8	17.8	119.0	15.4	11.5	3.9
2	3 635.3	18.1	118.9	15.4	11.5	3.9
3	3 625.8	17.9	119.0	15.5	11.5	4.0

Table 4. Uptake data* for tetrahydrofuran solutions of $[MnI_2L]$ complexes at *ca.* −65 °C

Complex	Concentration/mol dm^{-3}	Volume of gas mixture absorbed/cm^3
$[MnI_2(PPr^n_3)]$	1.54×10^{-2}	32.5
$[MnI_2(PBu^n_3)]$	1.69×10^{-2}	33.5
$[MnI_2(PPhMe_2)]$	1.47×10^{-2}	33.4
$[MnI_2(PPhEt_2)]$	1.73×10^{-2}	32.8

* Blank uptake = 33.0 cm^3.

Conclusions

The complexes $[MnX_2L]$ (X = Cl; L = PPr^n_3, PBu^n_3, $PPhMe_2$, or $PPhEt_2$; X = Br, L = PBu^n_3) react with ethylene in thf solution at 0 °C to give 1:1 adducts. None of the iodide complexes nor $[MnX_2(PPh_3)]$ (X = Cl, Br, or I) react with ethylene under these conditions. This order of stability of the ethylene adducts [*i.e.* Cl > Br > I, and $PR_3 > PPhR_2 > PPh_3$ (R = Me or Et)] is probably due to a combination of both steric and electronic effects. Thus, the order of decreasing stability follows the same order as decreasing ligand size and also the same order as decreasing electronegativity of the halide. If the electronic effect were the dominant factor this would imply that the σ component of the manganese(II)–ethylene bond is more important than the π component, since the increasing electron-withdrawing ability of the halide will promote donation of electron density from ethylene, thereby increasing the strength of the manganese(II)–ethylene σ bond.

As our investigations of small-molecule binding by the $[MnX_2L]$ complexes proceeds we increasingly observe the ability of these compounds to discriminate one gas from another. For example, recent investigations have shown that the ability of the $[MnX_2L]$ complexes to bind sulphur dioxide[7] varies as X = I > Br ≫ Cl, which contrasts vividly with the ethylene affinity, X = Cl > Br ≫ I. Moreover, in the 'inert' PPh_3 series of complexes only $[MnI_2(PPh_3)]$ will bind sulphur dioxide.

Experimental

All manipulations were performed under a dry argon atmosphere. Solvents were dried by published procedures.[9]

Preparation of thf Solutions of $[MnX_2L]$ *Complexes.—For* X = Cl *or* Br. A weighed quantity of powdered anhydrous[9] MnX_2 was added to a pre-dried argon-filled round-bottom flask (250 cm^2) fitted with a side arm and vacuum stopcock against a stream of argon. The flask was then evacuated and heated with a low Bunsen flame to ensure no moisture contamination had occurred. The vacuum was removed with dry argon and a magnetic stirrer was used to ensure the salt remained powdered. Freshly distilled thf was collected in another pre-dried argon-filled flask, and this flask was flushed several times to ensure no dioxygen contamination. A syringe was used to transfer the thf (10 cm^3) from this flask to the flask containing the halide, during which time argon was continually blown through both flasks. Once the thf had been transferred a vacuum was applied and then removed with argon. This was repeated several times. An equimolar quantity of the required phosphine was then added against a stream of argon. Vacuum was again applied and then removed with dry argon, several times. The slurry was stirred for *ca.* 1 week, after which time dry thf was added to give a solution of required concentration.

For X = I. The procedure for the preparation of the $[MnI_2L]$ complexes was essentially the same as that for $[MnX_2L]$ (X = Cl or Br) except that sufficient thf was added to give a solution of the required concentration before the addition of the phosphine.

Ethylene Uptake Measurements.—These were performed as previously described for sulphur dioxide.[7]

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