A Comparison of the Efficiencies of Polymer-supported Phosphine and Phosphine Oxide Complexes of Manganese(II), $MnX_2($Ⓟ$C_6H_4PPh_2)$ and $MnX_2\{$Ⓟ$C_6H_4P(O)Ph_2\}_n$ (n = 2 or 4; X = Cl, Br, or I), for the Absorption of Sulphur Dioxide

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Diphenylphosphinated poly(styrene–divinylbenzene), Ⓟ$C_6H_4PPh_2$ (L), reacts readily with the manganese(II) salts, MnX_2 (X = Cl, Br, or I) under anhydrous conditions to form $MnX_2(L)_n$ (X = Cl or Br, n = 1; X = I, n = 1.5). The similar reaction of the phosphine oxide, Ⓟ$C_6H_4P(O)Ph_2$ (L'), affords the complexes $MnX_2(L')_n$ (X = Cl, n = 1; X = Br or I, n = 1.5) and $MnX_2(L')_m$ (X = Cl or Br, m = 3; X = I, m = 5), depending upon reaction conditions. Both the phosphine and phosphine oxide complexes absorb SO_2 either when suspended in a mixture of toluene and dichloromethane (60:40 v/v), or in the solid state. In both cases the efficiencies are found to be in the order I > Br ~ Cl. Sulphur dioxide binding is irreversible for the phosphine complexes, but partially reversible with phosphine oxide derivatives.

In recent years there has been a rapid growth in the use of polymer-supported metal complexes mainly as catalysts for hydrogenation, hydroformylation, hydrosilylation, and isomerization reactions.[1] Apart from the obvious advantage of ease of recovery the thermal stabilities of such complexes are frequently higher than those of their homogeneous counterparts and they are often less sensitive to oxidation and moisture.

Work in this Department has shown that manganese(II) complexes of certain phosphine and phosphine oxides have the ability to bind sulphur dioxide.[2,3] Thus, phosphine complexes of the type $[MnX_2(PR_3)]$ (X = I or Br, R = alkyl or aryl) react irreversibly with SO_2 to give the complexes $[MnX_2(PR_3)(SO_2)_{0.66}]$,[2] while the phosphine oxide complex $[MnI_2(OPPh_3)_4]$ reacts with SO_2 by insertion into the Mn–I bonds giving $[Mn(O_2SI)_2(OPPh_3)_4]$.[3] When this last compound is heated or subjected to a vacuum for 2—3 h one of the SO_2 molecules is removed to give $[MnI(O_2SI)(OPPh_3)_4]$.[3] This reversibility of the SO_2 insertion is of some interest and possible application of manganese(II) complexes for the removal of SO_2 from industrial waste gas emissions can be envisaged. In an effort to improve the chemical robustness of the complexes we have synthesized a number of polymer-supported phosphine and phosphine oxide manganese derivatives and compared their behaviour with sulphur dioxide.

Results and Discussion

Beads of the commercially available 1% styrene–divinylbenzene co-polymer (BIO-BEADS S-X1) were brominated (Br_2, $AlBr_3$) and diphenylphosphinated [$LiPPh_2$ in tetrahydrofuran (thf)] by previously reported procedures[4] to give samples which contained 9.4% phosphorus. The phosphinated polymer was then caused to react under anhydrous conditions with the manganese(II) salts, MnX_2 (X = Cl, Br, or I) in a 1:1 molar ratio to give the supported complexes (**1**)—(**3**). After thorough washing to remove any uncomplexed manganese salts, analysis (Table 1) indicated an approximate 1:1 phosphorus:manganese ratio where X = Cl and Br; complexation to MnI_2 appears to be less efficient.

Oxidation of the phosphinated polymer with peracetic acid gave the corresponding phosphine oxide (P, 8.8%), which reacted with the manganese salts (2:1 polymer:Mn ratio) to give the supported complexes (**4**)—(**6**). Microanalysis (Table 1), after thorough washing, indicates the unusual stoicheiometry of $MnX_2[$Ⓟ$C_6H_4P(O)Ph_2]_{1.2-1.4}$, for X = Cl, Br, or I, which closely resembles the stoicheiometry of 1.5:1 found for the silica-supported complex $MnI_2[Ph_2P(O)CH_2CH_2Si(O\text{–})_3]_{1.5}$.[5]

When the ratio of supported phosphine oxide ligand to manganese salts was increased to 4:1 the complexes (**7**)—(**9**) were obtained. The chloro and bromo derivatives, (**7**) and (**8**) respectively, have the approximate stoicheiometry of $MnX_2[$Ⓟ$C_6H_4P(O)Ph_2]_{3.0-3.1}$, while for the iodo complex the P:Mn ratio is much higher.

Reactions with Sulphur Dioxide.*—A rapid colour change occurs when the phosphine complexes (**1**)—(**3**) are exposed to an atmosphere of sulphur dioxide, either when suspended in a mixture of toluene and CH_2Cl_2, or in the solid state. The uptake of SO_2 is higher in the solid state than when a solvent is used, and gas absorption is usually complete after *ca.* 30 min. An estimate of efficiency is the S:Mn ratio (Table 2). These figures are only available for the reactions carried out in a solvent, but they show quite clearly that the order of efficiency is I > Br ~ Cl. Assuming co-ordination of one SO_2 molecule per Mn atom, then for the iodo derivative more than half of the available Mn atoms are co-ordinated to an SO_2 molecule, and this figure is even higher when the reaction is carried out in the absence of a solvent. When the complexes (**10**)—(**12**) are subject to a high vacuum for several hours there is only a small reduction in the sulphur content, possibly due to loss of SO_2 trapped in the polymer matrix, and it would appear that SO_2-binding in these complexes is irreversible, as found previously for $[MnX_2(PR_3)(SO_2)]$ (X = I or Br).[2,3] This contrasts with the behaviour of the silica-supported analogue $MnI_2(Ph_2PCH_2CH_2\text{•sil})(SO_2)$ in which the SO_2 binding is partially reversible.[5]

The supported phosphine oxide complexes (**4**)—(**9**) also absorb sulphur dioxide with a noticeable colour change in most cases to give the adducts (**13**)—(**18**). From the results presented in Table 3 it can be seen that the efficiencies are again greatest for the iodide complexes, and the complexes (**7**)—(**9**) are superior to (**4**)—(**6**). The iodo complex (**9**) absorbs almost two

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* At least three repeat determinations were performed for each uptake experiment. Reproducibility varied in the range 3—7%.

Table 1. Analytical data for the phosphine, Ⓟ$C_6H_4PPh_2$ (L), and phosphine oxide, Ⓟ$C_6H_4P(O)Ph_2$ (L′), complexes

			Analysis (% Found)					
Reaction	Compound	Colour	C	H	P	Mn	P/Mn ratio	Formula assigned
$MnCl_2$ + L	**(1)**	Grey	48.4	4.3	6.4	10.2	1.1	$MnCl_2(L)$
$MnBr_2$ + L	**(2)**	Buff	43.1	3.8	6.2	9.8	1.1	$MnBr_2(L)$
MnI_2 + L	**(3)**	Light pink	51.7	3.2	5.5	6.2	1.6	$MnI_2(L)_{1.5}$
$MnCl_2$ + 2L′	**(4)**	Off-white	59.3	4.9	5.4	7.7	1.2	$MnCl_2(L')$
$MnBr_2$ + 2L′	**(5)**	Brown	55.4	4.4	5.6	7.0	1.4	$MnBr_2(L')_{1.5}$
MnI_2 + 2L′	**(6)**	Light brown	51.4	3.9	4.0	5.2	1.4	$MnI_2(L')_{1.5}$
$MnCl_2$ + 4L′	**(7)**	Off-white	68.1	5.1	7.4	4.2	3.1	$MnCl_2(L')_3$
$MnBr_2$ + 4L′	**(8)**	Grey	63.6	4.6	5.7	3.3	3.1	$MnBr_2(L')_3$
MnI_2 + 4L′	**(9)**	Deep yellow	63.7	5.0	7.6	2.7	5.0	$MnI_2(L')_5$

Table 2. Analytical data for the adducts **(10)**—**(12)** of sulphur dioxide and the phosphine manganese(II) complexes

				Found (%)[a]					
Reaction	Product	Colour		C	H	Mn	P	S	SO_2/Mn ratio[b]
(1) + SO_2	**(10)**	Bright yellow	(i)	48.8	4.1	9.2	5.2	1.6	0.3
			(ii)	47.8	4.1	—	2.1	2.0	
(2) + SO_2	**(11)**	Bright yellow	(i)	42.4	3.9	8.5	4.8	1.2	0.24
			(ii)	38.6	3.9	—	—	1.8	
			(iii)	39.5	4.1	—	—	1.5	
(3) + SO_2	**(12)**	Deep red	(i)	38.0	3.2	4.3	4.0	1.4	0.56
			(ii)	35.4	3.4	—	—	3.5	
			(iii)	37.5	3.6	—	—	2.8	

[a] (i) Suspension in toluene–CH_2Cl_2 (60:40 v/v); (ii) in the solid state; (iii) after application of a vacuum (0.01 mmHg, *ca.* 1.33 Pa) for several hours.
[b] Corrected values = $55(S_{found})/32(Mn_{found})$.

molecules of SO_2 per Mn atom to form **(18)**, and this agrees well with the previous observation that $[MnI_2(OPPh_3)_4]$ reacts with SO_2 to give the insertion product $[Mn(O_2SI)_2(OPPh_3)_4]$. In the case of these phosphine oxide derivatives **(13)**—**(18)** the evidence is more convincing that the binding of the SO_2 is partially reversible. Certainly the iodo complex **(18)** appears to lose one of the SO_2 molecules under high vacuum.

The Nujol-mull i.r. spectra of the complexes and of the sulphur dioxide adducts were ill defined and generally weak. It was clear that the SO_2 adducts did have absorptions (*ca.* 1 150 cm^{-1} for the complexes of phosphine oxide ligands)[6] not present in the original complexes; however it is not possible to determine unambiguously the nature of the Mn–SO_2 interaction on this basis.

Experimental

The polymer support used in this work was a commercial sample of 1% styrene–divinylbenzene copolymer (200—400 mesh, Bio Rad Laboratories SX-1), which was brominated (Br_2, $AlBr_3$ in nitromethane), and diphenylphosphinated ($LiPPh_2$ in thf) according to previously reported procedures.[4] The phosphinated polymer gave the following elemental analysis results (Found: C, 82.9; H, 6.1; Br, 0.4; P, 9.4. Calc. for $C_{20}H_{17}P$; C, 83.3; H, 5.9; Br, 0.0; P, 10.75%) after washing with methanol and dichloromethane followed by heating under vacuum at 100 °C for 16 h.

Preparation of the Phosphine Oxide.—Freshly prepared peracetic acid (40% in acetic acid, 70 cm^3) was added slowly to a suspension of the phosphinated polymer (53.45 g) in a mixture of dichloromethane (50 cm^3) and acetic acid (50 cm^3) and the mixture was stirred at room temperature for 3 h. The beads were filtered off, washed with methanol and dichloromethane, and finally dried at 100 °C *in vacuo* over 16 h to give the oxide (57.60 g) (Found: C, 74.5; H, 5.7; P, 8.8. Calc. for $C_{20}H_{17}OP$: C, 78.9; H, 5.6; P, 10.2%).

General Procedure for the Preparation of Manganese(II) *Complexes.*—All reactions were carried out in a one-necked 250-cm^3 flask equipped with a tapped side-arm. The flask was flame-dried with a stream of dry argon before addition of the anhydrous manganese salt (4.0 mmol). The flask was then evacuated and the solid stirred magnetically to produce a fine powder which was warmed gently under vacuum to remove the last traces of moisture. The desired molar quantity of the polymer-supported ligand was then introduced under an argon atmosphere followed by a 1:1 mixture of dry, freshly distilled and degassed tetrahydrofuran and n-pentane. The flask was evacuated, followed by introduction of argon and this cycle was repeated four times to ensure that all traces of air were removed. The mixture was then stirred under argon at room temperature for 5 d, before filtration of the solid (Schlenk technique) under argon, followed by drying under vacuum. The results are given in Table 1.

General Procedure for Reaction of the Manganese(II) *Complexes with Sulphur Dioxide.*—(*a*) *In suspension.* The apparatus and the drying procedure used were as described in the previous experiment. The supported manganese(II) complex was introduced into the flask under an atmosphere of dry nitrogen. The solid was then finely powdered by stirring and warming gently under vacuum. A mixture of dry, freshly distilled and degassed toluene and dichloromethane (60:40 v/v) was introduced under argon, and the cycle of evacuation followed by introduction of argon was repeated four times. The flask was finally evacuated and dry sulphur dioxide was introduced from a vacuum system. There was a rapid uptake of gas during the initial 10—15 min and, in many cases, an obvious colour change was observed. The subsequent uptake of gas was very slow. After stirring for

Table 3. Analytical data for the adducts (**13**)—(**18**) of sulphur dioxide and the manganese(II) phosphine oxide complexes

				Found (%)[a]					
Reaction	Product	Colour		C	H	Mn	P	S	SO_2/Mn ratio[b]
(**4**) + SO_2	(**13**)	White	(i)	59.3	4.7	8.4	6.0	1.0	0.2
			(ii)	48.9	3.9	—	—	1.0	
			(iii)	40.0	4.0	—	—	0.2	
(**5**) + SO_2	(**14**)	Grey	(i)	53.9	4.0	7.6	6.5	0.7	0.16
			(ii)	34.4	3.4	—	—	0.3	
(**6**) + SO_2	(**15**)	Deep red	(i)	47.0	3.7	5.4	5.4	2.6	0.83
			(ii)	45.1	3.6	—	—	2.7	
			(iii)	59.3	4.2	—	—	1.0	
(**7**) + SO_2	(**16**)	Pale yellow	(i)	65.0	5.3	4.5	6.3	2.0	0.76
			(ii)	64.4	5.0	—	—	1.5	
(**8**) + SO_2	(**17**)	Pale yellow	(i)	64.3	4.9	3.5	6.8	1.0	0.49
			(ii)	56.8	4.2	—	—	0.7	
			(iii)	63.3	4.7	—	—	0.6	
(**9**) + SO_2	(**18**)	Orange	(i)	55.4	4.3	2.7	6.3	3.0	1.91
			(ii)	59.6	4.4	—	—	2.2	
			(iii)	72.0	5.4	—	—	1.1	

[a] (i) Suspension in toluene–CH_2Cl_2 (60:40 v/v); (ii) in the solid state; (iii) after application of a vacuum (0.01 mmHg) for several hours. [b] Corrected values = $55(S_{found})/32(Mn_{found})$.

several days at room temperature the product was filtered off and stored under vacuum at room temperature. The results are presented in Tables 2 and 3.

(*b*) *In the solid state.* Using the same procedure sulphur dioxide was introduced into the flask containing only the dry, powdered manganese(II) complex and the uptake of gas was monitored. Gas absorption occurred over 30 min and was accompanied by a noticeable colour change. The solid was stirred under sulphur dioxide for 16 h, and was then stored under vacuum at room temperature. The results are presented in Tables 2 and 3.

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