The preparation, characterisation and subsequent reaction with sulfur dioxide of some triphenylarsine oxide complexes of manganese(II) salts

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Abstract

A number of manganese(II) complexes of the type $Mn(OAsPh_3)_nX_2$ (X = Cl, Br, I, NCS; n = 1, 2, 3 or 4) have been prepared and characterised, but the successful preparation of some of them has been found to be solvent dependent. For example, $Mn(OAsPh_3)_2I_2$ may be synthesised in toluene or acetone, but $Mn(OAsPh_3)_3I_2$ will not form in acetone and either ethyl acetate or toluene must be used. Also reported is the first crystallographically characterised manganese(II)/arsine oxide complex, $Mn(OAsPh_3)_2Cl_2$, which is found to have a pseudo-tetrahedral monomeric structure. A wide spectrum of reactivity towards sulfur dioxide of these complexes slurried in toluene was observed. Thus, for X = Cl, Br, NCS, or the mono ligand complexes only $Mn(OAsPh_3)Br_2$ forms a 1:1 SO_2 adduct, whereas all the bis ligand complexes form 1:1 adducts, as does $Mn(OAsPh_3)_3(NCS)_2$. $Mn(OAsPh_3)_nI_2$ (n = 2, 3) appear to undergo a complex redox reaction with SO_2 to produce materials containing sulfate and where the Ph_3AsO has been reduced to Ph_3As. From many of the filtrates from these reactions can be isolated the sulfuric acid derivative $(Ph_3AsOH)HSO_4$.

Introduction

Sulfur dioxide is a serious environmental pollutant and it is therefore necessary to develop effective methods for its removal, preferably by employing a reusable absorber; for this reason and for scientific curiosity we have for several years been investigating the binding and activation of sulfur dioxide by a wide range of transition metal complexes. The initial work began with the observation that complexes of the general formula $Mn(PR_3)X_2$ bind a variety of small molecules, including SO_2 [1]. This led to the investigation of other manganese(II) complexes and their reaction with SO_2. In particular, phosphine oxide complexes of MnX_2 salts (X = Cl, Br, I, NCS, NO_3 and ClO_4) have been studied [2–7]. One complex of particular interest was $Mn(OPPh_3)_4I_2$ which coordinates two SO_2 moieties by a novel SO_2 insertion into the Mn–I bonds to form $[Mn(OPPh_3)_4\{OS(O)I\}_2]$ [8]. Furthermore, the adduct exhibits demi-reversibility on heating and subsequent re-exposure to SO_2. In contrast, the analogous arsine oxide complex, $Mn(OAsPh_3)_4I_2$, reacts with SO_2 to form $[Mn(OAsPh_3)_3\{OS(O)I\}_2]$ in which a ligand has been

displaced [9]. Moreover, the SO_2 appears to be activated, since heating $[Mn(OAsPH_3)_3\{OS(O)I\}_2]$ *in vacuo* results in the formation of Ph_3AsI_2 [10, 11]. This is a most interesting observation of the reduction of Ph_3AsO to Ph_3As and its subsequent oxidation to form Ph_3AsI_2. This has led us to investigate other triphenylarsine oxide systems and we have as a preliminary attempted the preparation of the following complexes, $Mn(OAsPh_3)_nX_2$ (X = Cl, Br, I, NCS; n = 1–4). Some of these complexes have already been reported [12–16] but several are new, e.g. the mono and tris ligand complexes. We have discovered that the stoichiometry of the complex formed is frequently critically dependent on the nature of the anion, the solvent and the reaction temperature. Their reactivity towards adduct formation with sulfur dioxide also appears to be a subtle combination of ligand and anion, but with a marked tendency for iodide- and thiocyanate-containing complexes to be active to SO_2 binding [2–7].

Results and discussion

The earliest reported manganese(II)–triphenylarsine oxide complexes were formed by reacting the chloride

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or bromide salts with the ligand in stoichiometric ratios [16]. Goodgame and co-workers [12–14] have suggested from electronic spectra, magnetic susceptibilities and EPR spectra that the $Mn(OAsPh_3)_2X_2$ (X = Cl or Br) complexes have essentially tetrahedral structures while the $Mn(OAsPh_3)_4X_2$ (X = NCS or I) series are pseudo-octahedral. This evidence has been supported by X-ray powder diffraction but until now no crystal structures were available for manganese(II) complexes with triphenylarsine oxide. Thus the structure of $Mn(OAsPh_3)_2Cl_2$ reported here represents the first crystallographically characterised manganese(II)/arsine oxide complex. This structure confirms the hitherto proposed monomeric pseudo-tetrahedral structure for the bis complexes.

The complexes $Mn(Ph_3AsO)_2X_2$ (X = Cl, Br, NCS) and $Mn(Ph_3AsO)_4X_2$ (X = I, NCS) have previously been prepared by mixing MnX_2 and Ph_3AsO in the appropriate ratio in hot ethanol [15]. This method in our hands failed to produce pure $Mn(Ph_3AsO)_2I_2$, but our new method of preparation, which involves slurrying the appropriate ratios of reactants in toluene, did yield a pure product. We also obtained the novel mono complexes, $Mn(Ph_3AsO)X_2$ (X = Cl, Br, NCS), by this new method but failed to isolate $Mn(OAsPh_3)I_2$. The importance of the solvent used is illustrated by the preparation of our novel tris complexes, $Mn(OAsPh_3)_3I_2$ and $Mn(OAsPh_3)_3(NCS)_2$. The former is readily prepared (in toluene or ethyl acetate but not in acetone), either by directly reacting three moles of ligand with one mole of manganese(II) iodide, or by adding excess ligand to the bis complex and isolating the resulting solid. In contrast, however, $Mn(OAsPh_3)_3(NCS)_2$ could only be prepared in acetone.

The fifth new complex which we have prepared is $Mn(Ph_3AsO)_4Br_2$. The corresponding iodide and thiocyanate complexes are already known [14] but once again we have had to devise a new synthetic method for the bromo derivative. This involved stirring a mixture of $MnBr_2$ and excess Ph_3AsO in acetone at 0 °C overnight. Using this method to attempt to prepare the analogous tetrakis chloro complex yielded only the bis complex instead.

The physical properties and elemental analyses and some IR spectral bands for all the compounds prepared are listed in Tables 1 and 2. With the exception of the $\nu(CN)$ absorptions, the IR spectra of the complexes are very similar. However, since the manganese halides themselves show little IR activity in the 4000–400 cm^{-1} region, this is not unexpected. With the thiocyanate complexes a little more structural information can be obtained by comparing them with the corresponding phosphine oxide complexes [2]. The data suggest that with the exception of the tetrakis complexes the arsine oxide and phosphine oxide complexes do not have

similar structures. $Mn(OPPh_3)_4(NCS)_2$ has been crystallographically characterised as having a monomeric pseudo-octahedral structure [2]. It has a single $\nu(CN)$ at 2065 cm^{-1} which has been assigned to terminal N-bonded NCS. Since $Mn(OAsPh_3)_4(NCS)_2$ has a single $\nu(CN)$ at 2058 cm^{-1} this, too, has been assigned to terminal N-bonded NCS. Thus, we propose a monomeric pentacoordinate structure with terminal NCS groups for $Mn(OAsPh_3)_3(NCS)_2$ since it exhibits only a single $\nu(CN)$ absorption at 2060 cm^{-1}. This is in contrast to $Mn(OPPh_3)_3(NCS)_2$ which shows bridging and terminal NCS (2100 and 2060 cm^{-1}) and for which a dimeric structure has been proposed [2]. The reasons for these structural differences are not known with certainty but must be related to differences in physical properties of the triphenylphosphine oxide and triphenylarsine oxide ligands. Steric effects may be important since Ph_3PO has a greater cone angle than Ph_3AsO, although such effects are much less significant when compared with the corresponding triphenylphosphine and triphenylarsine ligands. Ph_3AsO is also more basic than Ph_3PO and thus would be expected to bind more strongly to the manganese centre.

The bis complex, $Mn(OAsPh_3)_2(NCS)_2$, shows two $\nu(CN)$ absorptions but the higher one (at 2100 cm^{-1}) is merely a shoulder on the main peak and may not be significant. This suggests that $Mn(OAsPh_3)_2(NCS)_2$ is a four-coordinate monomer like $Mn(OAsPh_3)_2Cl_2$ (see 'Crystallographic studies') and not a dimer like $[Mn(OPPh_3)_2(NCS)(\mu\text{-NCS})]_2$ [2]. The mono complex, $Mn(OAsPh_3)(NCS)_2$, has a strong absorption at 2090 cm^{-1}, probably due to bridging NCS in a short chain, as has been observed in $[Mn(OPPh_3)_2(NCS)_2]$. Bridging NCS groups in a polymer chain have $\nu(NCS)$ absorptions at 2124 and 2106 cm^{-1} [17]. No structural information could be obtained from the $\nu(CS)$ and $\delta(NCS)$ bands, since these are obscured by ligand absorptions.

The magnetic moments for the bis, tris and tetrakis thiocyanate complexes are close to the spin-only value expected, but the value of 5.50 $\mu\beta$ for the mono complex supports the proposed bridged structure, with the antiferromagnetic interactions being transmitted across the thiocyanate bridges. Thus, from the IR and magnetic data it seems likely that $Mn(OAsPh_3)(NCS)_2$ is dimeric, while $Mn(OAsPh_3)_2(NCS)_2$, $Mn(OAsPh_3)_3(NCS)_2$ and $Mn(OAsPh_3)_4(NCS)_2$ are four-, five- and six-coordinate monomers, respectively.

Crystallographic studies

The molecular structure of $Mn(OAsPh_3)_2Cl_2$, together with the atomic numbering scheme is shown in Fig. 1. Atomic coordinates and selected bond lengths and angles are given in Table 3. The molecule is a pseudo-tetrahedral monomer with the manganese atom co-

TABLE 1. Physical properties and elemental analyses for Mn(OAsPh$_3$)$_n$X$_2$

Complex	Colour	m.p. (°C)	μ ($\mu\beta$)	Anal.: found (calc.) (%)		
				C	H	X[a]
Mn(OAsPh$_3$)Cl$_2$	white	150	5.82	47.9(48.2)	3.6(3.3)	15.6(15.8)
Mn(OAsPh$_3$)$_2$Cl$_2$	white	228	6.07	56.4(56.1)	3 7(3.9)	9.1(9.2)
Mn(OAsPh$_3$)Br$_2$	white	109–112	5.77	38.7(40.2)	3.6(2.8)	29.2(29.8)
Mn(OAsPh$_3$)$_2$Br$_2$	white	157–159	6.08	51.2(50.3)	3.4(3.5)	17.9(18.6)
Mn(OAsPh$_3$)$_4$Br$_2$	white	162–164	5.70	57.2(57.5)	3.9(4.0)	10.9(10.6)
Mn(OAsPh$_3$)$_2$I$_2$	yellow	180–184	5.86	45.2(45 3)	3.1(3.1)	26.2(26.7)
Mn(OAsPh$_3$)$_3$I$_2$	yellow	151–155	5.78	49.5(50.8)	3.5(3.5)	19.5(19.9)
Mn(OAsPh$_3$)$_4$I$_2$	yellow	214–218	5.97	54.4(54.1)	3 8(3.8)	15.2(15.9)
Mn(OAsPh$_3$)(NCS)$_2$	white	210	5.50	48.4(48.7)	2 8(3.0)	5.5(5.7)
Mn(OAsPh$_3$)$_2$(NCS)$_2$	white	168–174	5.90	55.4(55.9)	3.7(3.7)	3.1(3.4)
Mn(OAsPh$_3$)$_3$(NCS)$_2$	grey	222–226	5.91	59.1(59.1)	3.9(4.0)	2.0(2.5)
Mn(OAsPh$_3$)$_4$(NCS)$_2$	white	220	6.10	61.6(61.0)	4.2(4.1)	1.8(1.9)

[a]Halogen or nitrogen.

TABLE 2. IR data for Mn(OAsPh$_3$)$_n$X$_2$ complexes; all values in cm^{-1}

Complex	ν(CN)	ν(AsO)
Mn(OAsPh$_3$)Cl$_2$		920, 900
Mn(OAsPh$_3$)$_2$Cl$_2$		920, 900
Mn(OAsPh$_3$)Br$_2$		910, 885
MN(OAsPh$_3$)$_2$Br$_2$		910, 890
Mn(OAsPh$_3$)$_4$Br$_2$		895, 875
Mn(OAsPh$_3$)$_2$I$_2$		910, 885, 870
Mn(OAsPh$_3$)$_3$I$_2$		900, 870
Mn(OAsPh$_3$)$_4$I$_2$		895, 870
Mn(OAsPh$_3$)(NCS)$_2$	2090(s), 2060(sh)	900, 880
Mn(OAsPh$_3$)$_2$(NCS)$_2$	2100(sh), 2055(s)	895, 875
Mn(OAsPh$_3$)$_3$(NCS)$_2$	2060	898, 878
Mn(OAsPh$_3$)$_4$(NCS)$_2$	2058	895, 875

Fig. 1. The molecular structure and atom numbering scheme for Mn(OAsPh$_3$)$_2$Cl$_2$ (H atoms omitted for clarity).

ordinated to two terminal chlorine atoms and the oxygen atoms of two triphenylarsine oxide ligands.

Reaction with Sulfur Dioxide

The reaction of SO$_2$ with the Mn(OAsPh$_3$)$_n$X$_2$ complexes has been studied in toluene slurries. The products from these reactions, their physical properties and elemental analyses are shown in Table 4, whilst the IR data are shown in Table 5. The absence of ν(SO) in the spectra of some of the complexes may be because the bound SO$_2$ is readily released once the SO$_2$ atmosphere has been removed. This would also explain the small amount of sulfur found in the elemental analyses (see footnote to Table 4).

(i) X=Cl, Br or NCS

It can be seen that for the mono ligand complexes only the bromo derivative reacted with SO$_2$. The sulfur analysis is low but carbon and hydrogen analyses correspond to the uptake of one mole of SO$_2$. The TGA of the adduct showed a low-temperature mass change
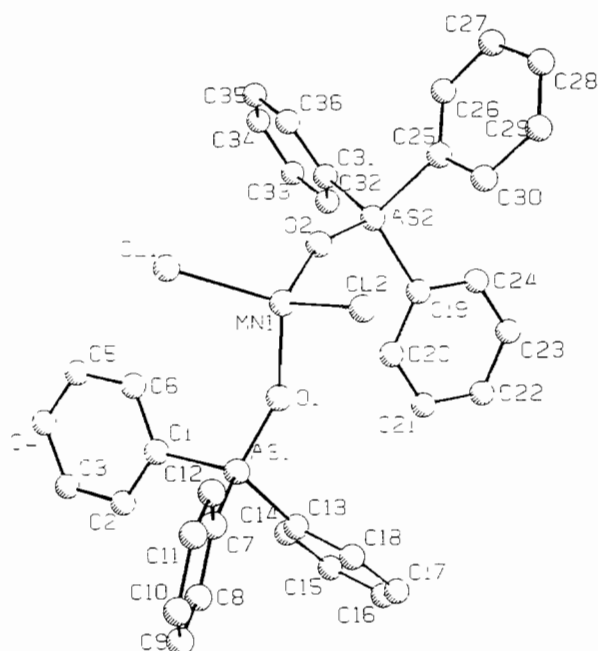
corresponding to the loss of one mole of SO$_2$. However, all of the bis complexes form 1:1 adducts with SO$_2$, as determined by elemental and thermogravimetric analyses, Table 6. This is in marked contrast to the analogous Ph$_3$PO complexes where only the chloro complex reacts with SO$_2$ [6]. The tris thiocyanate complex forms a 1:1 adduct, as does its Ph$_3$PO counterpart, but Mn(OAsPh$_3$)$_4$(NCS)$_2$, unlike Mn(OPPh$_3$)$_4$(NCS)$_2$ [2], does not form a simple stoichiometric adduct. The product does contain SO$_2$, as shown by ν(SO) at 1260 cm^{-1} but the analysis does not correspond to a simple formula. A strong IR band at *c.* 1250 cm^{-1}, exhibited by most of the complexes studied here, see Table 5,

TABLE 3. Selected bond lengths and angles for $Mn(OAsPh_3)_2Cl_2$

Bond lengths (Å)		Bond angles (°)	
Mn(1)–O(1)	2.025(3)	Cl(1)–Mn(1)–O(1)	110.57(9)
Mn(1)–O(2)	1.989(3)	Cl(1)–Mn(1)–O(2)	111.6(1)
Mn(1)–Cl(1)	2 342(1)	Cl(2)–Mn(1)–O(1)	109.0(1)
Mn(1)–Cl(2)	2 345(1)	Cl(2)–Mn(1)–O(2)	112.3(1)
As(1)–O(1)	1.668(3)	Cl(1)–Mn(1)–Cl(2)	111.08(5)
As(2)–O(2)	1.664(3)	O(1)–Mn(1)–O(2)	102 0(1)

TABLE 4 Physical properties and elemental analyses of the products from the reaction of $Mn(OAsPh_3)_nX_2$ with sulfur dioxide

Reaction	Product	Colour	m p. (°C)	Anal.: found (calc.)			
				C	H	X[a]	S
$Mn(OAsPh_3)Cl_2 + SO_2$	$Mn(OAsPh_3)Cl_2$	white	150	48.6(48.2)	3 8(3.3)		
$Mn(OAsPh_3)_2Cl_2 + SO_2$	$Mn(OAsPh_3)_2Cl_2(SO_2)$	cream	182–184	51.6(51.7)	3 6(3.6)	7.5(7.8)	2.1(3.8)
$Mn(OAsPh_3)Br_2 + SO_2$	$Mn(OAsPh_3)Br_2(SO_2)$	white	116–120	36 6(35.9)	2.9(2.5)		0.9(5.3)
$Mn(OAsPh_3)_2Br_2 + SO_2$	$Mn(OAsPh_3)_2Br_2(SO_2)$	cream	140–145	46.7(46.8)	3.3(3.3)		0.4(3.5)
$Mn(OAsPh_3)_4Br_4 + SO_2$	$Mn(OAsPh_3)_3Br_2(SO_2)$	beige	146	51.8(52.0)	2 6(3.6)	12 1(12.9)	1 4(2.5)
$Mn(OAsPh_3)_2I_2 + SO_2$	unknown	orange	120	29.1	2 4	17 5	5 9
$Mn(OAsPh_3)_3I_2 + SO_2$	unknown	orange	118	30.7	2.8	25.5	7.2
$Mn(OAsPh_3)_4I_2 + SO_2$	$Mn(OAsPh_3)_3I_2(SO_2)_2$	orange	140	44.9(46.2)	3.5(3.2)	18 4(18.1)	4.6(4 6)
$Mn(OAsPh_3)(NCS)_2 + SO_2$	$Mn(OAsPh_3)(NCS)$	white	215	48.6(48.7)	3 0(3.0)	5.6(5.7)	
$Mn(OAsPh_3)_2(NCS)_2 + SO_2$	$Mn(OAsPh_3)_2(NCS)_2(SO_2)$	cream	118–120	52.7(51.9)	3.6(3.4)	3.2(3 2)	5.8(10.9)
$Mn(OAsPh_3)_3(NCS)_2 + SO_2$	$Mn(OAsPh_3)_3(NCS)_2(SO_2)$	green	168	57.3(56.0)	4 0(3.8)	2.3(2.3)	6.1(8 0)
$Mn(OAsPh_3)_4(NCS)_2 + SO_2$	unknown	yellow	180	45.6	3 5	1.8	5.6

[a]Halogen or nitrogen. The proposed formulae are based on C, H, X and P analyses since the quantity of S found is consistently lower than expected. The lability of the SO_2 in many of these complexes means that it is often lost before it can be detected by the analytical technique employed. This method involves passing a stream of helium gas over the sample. Depending on the flow-rate of the gas, varying amounts of sulfur are detected. This purging procedure does not affect other elemental analyses For example, %C is determined from the initial weight of the samples and the amount of CO_2 detected. If SO_2 is lost after the initial weighing it does not affect the %C result

TABLE 5 IR data for SO_2 adducts; all values in cm^{-1}

Complex	$\nu(CN)$	$\nu(AsO)$	$\nu(SO)$
$Mn(OAsPh_3)_2Cl_2(SO_2)$		920, 900	1240
$Mn(OAsPh_3)Br_2(SO_2)$		910, 885	[a]
$Mn(OAsPh_3)_2Br_2(SO_2)$		910, 885	1260
$Mn(OAsPh_3)_3Br_2(SO_2)$		908, 880	1310, 1260
$Mn(OAsPh_3)_2I_2 + SO_2$			1160–1070, 650–550
$Mn(OAsPh_3)_3I_2 + SO_2$			1160–1070, 650–550
$Mn(OAsPh_3)_3I_2(SO_2)_2$		876	1248
$Mn(OAsPh_3)_2(NCS)_2(SO_2)$	2105(sh), 2100(sh), 2058(s)	900, 875	[a]
$Mn(OAsPh_3)_3(NCS)_2(SO_2)$	2050	875, 850	1308, 1260
$Mn(OAsPh_3)_4(NCS)_2 + SO_2$	2060	875	1260

[a]The absence of $\nu(SO)$ suggests that sulfur dioxide is lost on exposure to air.

is indicative of the insertion of sulfur dioxide into the metal–anion bond, crystallographically demonstrated earlier by Gott et al. [8].

(ii) X = I

Table 4 shows that, with the exception of $Mn(OAsPh_3)_4I_2$ (previously reported) [9], the reaction of $Mn(OAsPh_3)_nI_2$ with SO_2 in a toluene slurry yields products which, irrespective of the number of ligands in the original complex, have almost the same %C and %H. No formula has been proposed since the varying amounts of sulfur and iodine render this impossible. The TGA traces for these products show 'simple' decomposition just above room temperature without the initial loss of a volatile component. The IR spectra show no $\nu(AsO)$, so presumably Ph_3AsO has been

TABLE 6. Thermogravimetric analyses of $Mn(OAsPh_3)_nX_2(SO_2)$ complexes

Complex	Mass of sample (mg)	Mass loss (mg)	Moles of SO_2 lost	Temperature of SO_2 loss (°C)
$Mn(OAsPh_3)Br_2(SO_2)$	7.4	0.9	1.16	20–90
$Mn(OAsPh_3)_2Cl_2(SO_2)$	5.6	0.5	1.18	20–110
$Mn(OAsPh_3)_2Br_2(SO_2)$	7.2	0 6	1.22	20–135
$Mn(OAsPh_3)_2(NCS)_2(SO_2)$	8.3	0.6	0.99	20–115

reduced to Ph_3As. The spectra show broad absorptions in the 1160–1070 and 650–550 regions which can be assigned to $\nu(SO)$ of sulfate [18]. In the absence of air and moisture the ligand is the only possible oxygen donor to sulfur dioxide. This agrees with the absence of $\nu(AsO)$ in the IR spectra. We have previously observed [9–11] that manganese-bound SO_2 appears to be activated and easily reduces Ph_3AsO to form Ph_3AsI_2. Whilst the reduction of organoarsenic(V) oxides to organoarsine(III) compounds in strongly acidic media is well-known, [19], our present observations suggest that manganese activation of SO_2 greatly assists this process.

Exposing the filtrates of these reactions to the atmosphere resulted in the formation of straw-coloured crystals which analysed as $Ph_3AsO \cdot H_2SO_4$. (Anal. Found: C, 51.4; H, 4.1; SO_4, 22.6. Calc.: C, 51.4; H, 4.0; SO_4, 22.9%.) Single crystal X-ray analysis on similar crystals isolated from the filtrate of an Fe(III)/Ph_3AsO reaction with SO_2 shows them to be $(AsPh_3OH)(HSO_4)$ [20]. Oxidation of sulfur dioxide to sulfuric acid has also been observed to occur in the filtrates of many of the corresponding phosphine oxide reactions and in a mixed phosphine oxide/arsine oxide reaction. Single crystal X-ray analysis has identified (Ph_3PO)-$(Ph_3POH)(HSO_4)$ [2] and $(Ph_3PO)(Ph_3AsO)$-(H_2SO_4) [21] in which two ligands are hydrogen-bonded to the sulfuric acid. The mechanism of formation of these crystals is unclear, but the observation points to a complex redox system involving the activation of manganese-bound sulfur dioxide.

Experimental

Preparation of complexes

(i) $Mn(OAsPh_3)X_2$ (X = Cl, Br, NCS)

The mono complexes $Mn(OAsPh_3)X_2$ (X = Cl, Br, NCS) were prepared by reacting the anhydrous manganese(II) salt with triphenylarsine oxide in the appropriate molar ratio. The preparation of $Mn(OAsPh_3)Cl_2$ is typical and is described below. Anhydrous $MnCl_2$ (1.26 g, 10 mmol) and Ph_3AsO (3.22 g, 10 mmol) were stirred together in dry toluene (50

cm^3) for c. one week. The resulting solid was filtered off, washed with toluene and dried in vacuo over P_2O_5.

(ii) $Mn(OAsPh_3)_n(NCS)_2$ (n = 2, 3, 4)

These complexes were prepared by mixing the ligand with $Mn(NCS)_2$ in acetone. The procedure is typified by the preparation of $Mn(OAsPh_3)_4(NCS)_2$. Triphenylarsine oxide (5.56 g, 20.0 mmol) and $Mn(NCS)_2$ (0.86 g, 5.0 mmol) were mixed in acetone (100 cm^3). The reaction mixture was heated to boiling and then cooled in an ice-bath. The crystalline product was filtered, washed with acetone and dried over P_2O_5.

(iii) $Mn(OAsPh_3)_2X_2$ (X = Cl, Br, I)

The synthesis of $Mn(OAsPh)_2Cl_2$ is typical and is outlined below. Anhydrous $MnCl_2$ (0.86 g, 6.8 mmol) and Ph_3AsO (4.68 g, 14.5 mmol) were stirred in hot ethanol (40 cm^3) for 30 min. Upon cooling, the solid complex precipitated. It was filtered, washed with ethanol and dried in vacuo over P_2O_5.

(iv) $Mn(OAsPh_3)X_2$ (X = Br, I)

The complexes $Mn(OAsPh_3)_4X_2$ (X = Br, I) were prepared by mixing the manganese(II) salt with the ligand in a 1:4.4 mol ratio. The preparation of $Mn(Ph_3AsO)_4I_2$ is described below. Anhydrous MnI_2 (3.68 g, 11.9 mmol) and Ph_3AsO (16.9 g, 52.5 mmol) were stirred in acetone (80 cm^3) at 0 °C for 30 min. The reaction mixture was kept at 0 °C overnight. The solid complex was filtered, washed with acetone and dried in vacuo over P_2O_5.

Reaction with sulfur dioxide

The apparatus employed was a round bottomed 250 cm^3 flask equipped with a side-arm containing a ground glass tap. Approximately 0.5 g of complex was added to the pre-dried argon filled flask, against a stream of argon. Freshly distilled toluene (50 cm^3) was then added to the flask, also against a stream of argon. A vacuum was applied and let down several times with dry argon to guard against oxygen contamination. Finally, the head space was evacuated and the vacuum let down with sulfur dioxide. The contents of the flask were saturated with sulfur dioxide, the flask sealed and the

mixture left to stir for *c*. 7 days. The product was isolated by standard Schlenk techniques.

Elemental analyses were performed by the UMIST microanalytical service. IR spectra were recorded as Nujol mulls between KBr plates in the range 4000–400 cm^{-1} on a Perkin-Elmer 598 IR spectrometer. Magnetic susceptibility measurements were determined using an Oxford Instruments Faraday balance. Thermogravimetric analyses were carried out on a Stanton Redcroft TG 750 thermobalance.

X-ray structure determination

Crystallographic measurements on $Mn(OAsPh_3)_2Cl_2$ were made on a Nicolet R3m diffractometer using graphite monochromatised Mo Kα radiation. Structure calculation was performed using the Nicolet SHELX TL program [22].

Crystal data for $Mn(OAsPh_3)_2Cl_2$

$C_{36}H_{30}As_2Cl_2O_2Mn$, $M = 770.32$, monoclinic, space group $P2_1/n$, $a = 18.274(2)$, $b = 10.354(1)$, $c = 19.816(3)$ Å, $\beta = 115.91(2)°$, $V = 3372(2)$ Å^3, $Z = 4$, $D_c = 1.517$ g/cm^3, $\mu = (Mo\ K\alpha) = 25.09$ cm^{-1}, $F(000) = 1548$, $R = 0.037$, $R_w = 0.032$.

The crystal structure of $Mn(OAsPh_3)_2Cl_2$ is illustrated in Fig. 1. The Mn–O bond lengths (2.025(3) and 1.989(3) Å) are unremarkable and, moreover, the As–O bond lengths (1.668(3) and 1.664(3) Å) are almost identical to that of the parent ligand Ph_3AsO [23] (1.657(4) Å). It is therefore certain that the As–O bond represents a double bond.

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