Manganese(II) Complexes containing the Phenyl Diphenylphosphinate Ligand and Their Reactivity with SO$_2$; the First Crystallographically Characterised Complex containing a Phosphinate Ligand†

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Complexes of manganese(II) with the rarely studied phenyl diphenylphosphinate ligand have been synthesised. Their isolation is solvent dependent: the bis(ligand) complexes, [Mn{OPPh$_2$(OPh)}$_2$X$_2$] (X = Cl, Br, I or NCS), are readily isolated, but the tetrakis derivatives are only isolated for X = I or NCS. The complex [Mn{OPPh$_2$(OPh)}$_4$I$_2$] co-ordinates two molecules of sulfur dioxide and one of these is readily displaced. In marked contrast to the isostructural OPPh$_3$ derivative, [Mn{OPPh$_2$(OPh)}$_4$(NCS)$_2$] shows no tendency to bind SO$_2$. The X-ray crystal structure of [Mn{OPPh$_2$(OPh)}$_4$(NCS)$_2$]·C$_6$H$_5$Me has been determined. The Mn–O–P angle is 167.5(0.5)°, much increased over the analogous OPPh$_3$ complex (147.5°); this difference is attributed to enhanced sp character of the oxygen donor atom in the phosphinate complex.

There is increasing interest in the binding of sulfur oxides by transition-metal species partly because of academic interest,[1,2] but also because of the insidious nature of acid rain, of which sulfur dioxide emissions are a prime cause. We have paid particular attention to the interaction of sulfur dioxide with manganese(II) complexes of triphenylphosphine- and triphenylarsine-oxides, and discovered that the reactivity is ligand and halide dependent.[3–7] Moreover, the mode of sulfur dioxide co-ordination is unusual, *e.g.* [Mn(OPPh$_3$)$_4$I$_2$] inserts two molecules of SO$_2$ into the Mn–I bonds to give [Mn(OPPh$_3$)$_4${OS(O)I}$_2$], a species from which one SO$_2$ may subsequently be lost by heating to 129 °C in a reversible process [equation (1)].

$$[\mathrm{Mn(OPPh_3)_4\{OS(O)I\}_2}] \underset{\mathrm{SO_2}}{\overset{129\ ^\circ\mathrm{C}}{\rightleftharpoons}} [\mathrm{Mn(OPPh_3)_4\{OS(O)I\}I}] + \mathrm{SO_2} \quad (1)$$

An extension of this work to another 3d^5 element, iron(III), yielded results which again showed that the ability to bind SO$_2$ was discriminated by changes in ligand, halide and even the reaction medium. The complexes isolated were of stoichiometry [FeL$_4${OS(O)X}$_2$][FeX$_4$] (L = OPPh$_3$, X = Br; L = OAsPh$_3$, X = Cl or Br).[8] From the reaction of these complexes with SO$_2$ in the presence of moist air, the sulfuric acid derivatives (PPh$_3$O)(PPh$_3$OH)(HSO$_4$) and (AsPh$_3$OH)(HSO$_4$) could be obtained.

We have further extended our investigations to examine manganese(II) complexes of the ligand phenyl diphenylphosphinate, OPPh$_2$(OPh). Apart from our interest in the possible co-ordination of SO$_2$ by these materials, we were also aware that very few examples of phosphinate ligand co-ordination to a metal have been reported. The complexes [Zr{OPPh$_2$(OPh)}$_2$Cl$_4$][9] and [Co{OPEt$_2$(OEt)}$_2$Cl$_2$][10] have received a little characterisation, whilst OPPhMe(OMe) has been complexed to a number of first-row transition-metal perchlorates.[11] However, prior to the work reported here, no complex containing a phosphinate ligand has ever been characterised by single-crystal X-ray diffraction.

Results and Discussion

The ligand phenyl diphenylphosphinate, OPPh$_2$(OPh), is an ester, but effectively functions as a phenoxy-substituted derivative of OPPh$_3$. It exhibits similar basicity to this much more common ligand, *vis.* pK_b OPPh$_2$(OPh) 3.18, OPPh$_3$ 3.72, and OPBu$^n_3$ 4.98.[12] Two prominent ν(PO) bands at 1222 and 1199 cm^{-1} are observed in the infrared spectrum, in contrast to the single stretch at 1195 cm^{-1} for OPPh$_3$.[13] This splitting has been alternatively attributed to metastable conformers induced by steric crowding[14] and to intermolecular hydrogen bonding.[15]

Manganese(II) *Complexes.*—The complexes were synthesised by slurrying anhydrous MnX$_2$ (X = Cl, Br, I or NCS) salts with stoichiometric ratios of ligand in toluene, diethyl ether or hexane. The MnX$_2$ salts are essentially insoluble in these solvents, whereas the OPPh$_2$(OPh) ligand dissolves readily. In each case the complexes formed have moderate to poor solubility in the solvents used, and as a result can be isolated in reasonable yields by standard Schlenk techniques.

Accurate elemental analyses can be obtained for all the complexes without recrystallisation, Table 1, although the complexes do dissolve in CH$_2$Cl$_2$ and ethanol. Anaerobic conditions are employed during the synthesis to prevent hydrolysis or hydration of the manganese(II) salts, but the final products are air stable. The bis(ligand) complexes, [Mn{OPPh$_2$(OPh)}$_2$X$_2$] (X = Cl, Br, I or NCS) are isolated from reactions of MnX$_2$ with ligand in a 1:2 ratio; there is no solvent dependence of the reaction.

The use of a 1:4 MnX$_2$:ligand ratio still only yields [Mn{OPPh$_2$(OPh)}$_2$X$_2$] for X = Cl or Br. Similarly, for this reaction stoichiometry only [Mn{OPPh$_2$(OPh)}$_2$I$_2$] is obtained using toluene or diethyl ether, but [Mn{OPPh$_2$(OPh)}$_4$I$_2$] can be isolated from hexane reactions. In contrast,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: atm = 101 325 Pa.

Table 1 Analytical and physical data for the complexes

Complex	Colour	M.p./ °C	ν(PO)[a]/cm^{-1}	μ_{eff}[b]	Λ[c]/ S cm^2 mol^{-1}	Analyses (%)[d] C	H	Hal/N	P	Mn
$[Mn\{OPPh_2(OPh)\}_2Cl_2]$	Pale green	159	1198, 1184s	6.03	2	59.8 (60.5)	4.1 (4.2)	9.8 (9.9)		
$[Mn\{OPPh_2(OPh)\}_2Br_2]$	Pale green	162	1198, 1181s	6.05	5	53.9 (53.8)	3.5 (3.7)	20.0 (19.9)	7.3 (7.8)	6.8 (6.8)
$[Mn\{OPPh_2(OPh)\}_2I_2]$	Pale yellow	177	1197, 1180 (sp)	6.04	13	48.2 (48.2)	3.5 (3.3)	28.1 (28.3)	6.6 (6.9)	5.9 (6.1)
$[Mn\{OPPh_2(OPh)\}_2(NCS)_2]$[e]	Green	112	1215, 1185m	5.73	8	60.0 (60.0)	3.8 (4.0)	3.7 (3.7)	8.5 (8.2)	6.6 (7.2)
$[Mn\{OPPh_2(OPh)\}_4I_2]$	Pale yellow	91	1222, 1198s	5.92	16	57.9 (58.2)	3.7 (4.0)	16.9 (17.1)	8.5 (8.4)	3.4 (3.7)
$[Mn\{OPPh_2(OPh)\}_4(NCS)_2]$[f]	Green	96	1222, 1192s	6.03	13	66.2 (66.0)	4.6 (4.5)	2.2 (2.1)	9.6 (9.2)	3.7 (4.1)

[a] ν(PO) 1222 and 1199s cm^{-1} for $OPPh_2(OPh)$. [b] At 293 K. [c] In nitrobenzene. [d] Calculated values in parentheses. [e] ν(CN) 2105m and 2060s cm^{-1}. [f] ν(CN) 2065s cm^{-1}

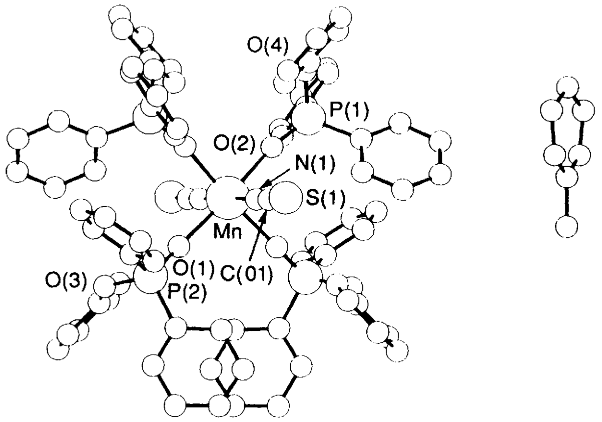

Fig. 1 The structure of $[Mn\{OPPh_2(OPh)\}_4(NCS)_2]{\cdot}C_6H_5Me$ with hydrogen atoms omitted for clarity

$[Mn\{OPPh_2(OPh)\}_4(NCS)_2]$ is the more thermodynamically favoured complex for not only can it be isolated from the 1:4 reactions in all three solvents, but it is also recovered as filtrate crystals from the 1:2 stoichiometry reactions.

All of the halide complexes (Table 1) exhibit spin-only magnetic moments, are essentially non-conducting in nitrobenzene and show shifts in ν(PO) as compared to the free ligand. The bis(ligand) complexes for X = halide are probably, therefore, pseudo-tetrahedral monomeric species, similar to those of the corresponding $[Mn(OPPh_3)_2X_2]$ (X = Cl, Br or I) complexes,[16–18] and $[Mn\{OPPh_2(OPh)\}_4I_2]$ probably has the *trans*-pseudo-octahedral structure previously assigned to $[Mn(OPPh_3)_4I_2]$.[19]

The parallels continue for the thiocyanato derivatives. The infrared spectrum of $[Mn\{OPPh_2(OPh)\}_2(NCS)_2]$ (Table 1) exhibits both terminal and bridging ν(CN) bands, comparable to those of $[Mn(OPPh_3)_2(NCS)_2]$.[3] The crystal structure of the latter shows it to be a five-co-ordinate dimer with both bridging and terminal anions. Both complexes exhibit a reduced room-temperature magnetic moment caused by antiferromagnetic superexchange through these bridges, and there can be little doubt that they have similar structures.

Crystallographic Study.—The complex $[Mn\{OPPh_2(OPh)\}_4(NCS)_2]$ was crystallised from toluene, resulting in the incorporation of toluene of crystallisation [Found (Calc.) for C_6H_5Me adduct: C, 66.9 (67.2); H, 4.5 (4.7); N, 2.1 (1.9); P, 8.6 (8.6)%]. The solvated yellow-green crystals produced identical ν(CN) and ν(PO) bands to those of the unsolvated complex.

The structure of $[Mn\{OPPh_2(OPh)\}_4(NCS)_2]{\cdot}C_6H_5Me$ together with the atomic numbering scheme for non-carbon/hydrogen atoms is shown in Fig. 1. Atomic coordinates and selected bond lengths and angles are given in Tables 2 and 3. A crystallographic two-fold axis bisects the molecule, resulting in *trans*-octahedral manganese(II) geometry. Intermolecular distances associated with the toluene are considerably longer than those required for bonding interactions. There is no evidence of intramolecular interaction between the phosphinato oxygen and *ortho* phenyl hydrogens, as proposed by Ohwada[15] from spectroscopic data, and all H • • • O distances exceed 2.40 Å, the sum of the van der Waals radii.

Generally, averaged bond lengths and angles are comparable with those of $[Mn(OPPh_3)_4(NCS)_2]$.[3] One unusual feature is the relatively open Mn–O–P bond angle. This is typically 147.5° for $[Mn(OPPh_3)_4(NCS)_2]$, similar to that in other crystallographically characterised complexes of manganese(II), cobalt(II) and copper(II) with triphenylphosphine oxide.[16–18,20–23]

The main bonding component in the metal–ligand interaction between first-row transition metals and $OPPh_3$ has been attributed to σ donation by a predominantly sp^2 oxygen.[24] The approximate nature of this approach is obvious, since a genuine sp^2 oxygen would give a 120° Mn–O–P angle. Hence, significant sp character must be imparted to raise the observed bond angle from its idealised value. Recent crystallographic studies of $Ph_3PO{\cdot}ECl_3$ (E = Al or Ga)[25] indicate that wholly sp-hybridised linear interactions can occur. Hence, the greater Mn–O–P angle in $[Mn\{OPPh_2(OPh)\}_4(NCS)_2]{\cdot}C_6H_5Me$ implies there is greater sp character in the donating oxygen. Presumably this is associated with the presence of the phenoxy substituent, although its precise effect is unclear.

A Referee has suggested that steric and packing effects could change the Mn–O–P angle significantly and that geometric distortion of the octahedral configuration would be easy in view of the d^5 configuration. However, the angles in Table 2 show that there is little distortion from O_h geometry at the metal, and the bonding is essentially normal. It is the Mn–O–P angle which is affected, although the Referee suggests that this may not be due to increasing sp hybridisation and that such hybridisation would affect all the angles in the ligand. However, there are two points against this argument. (*a*) The bonding in conventional M–O–P complexes is not totally sp^2 in character, since angles *ca.* 140–150° are observed, not 120°. To provide a bonding orbital on the oxygen at this angle some sp character must be introduced. (*b*) Secondly, linear bonding and sp hybridisation of the oxygen has been observed[25] for $Ph_3PO{\cdot}AlCl_3$. Significant changes in the other ligand angles were not observed in the structure of this adduct.

Reactions with Sulfur Dioxide.—The reactivity of the complexes towards sulfur dioxide has been examined in the solid state and also in SO_2-saturated slurries of diethyl ether and toluene. All the compounds except $[Mn\{OPPh_2(OPh)\}_4I_2]$ appear to be inert to SO_2 in the solid state, or in slurries, and no change in their infrared spectra or elemental analyses result from exposure to SO_2.

In contrast to this general inactivity, $[Mn\{OPPh_2(OPh)\}_4I_2]$ readily reacts with sulfur dioxide in the solid state and in slurries. Exposure of the yellow complex to SO_2 produces an orange adduct. When exposed to 1 atm of SO_2 a weight increase of 1.98 mol SO_2 per mol of complex is observed.

Table 2 Fractional atomic coordinates for non-hydrogen atoms of [Mn{$OPPh_2(OPh)\}_4(NCS)_2]\cdot C_6H_5Me$

Atom	*x*	*y*	*z*
Mn	0.000 00	0.000 0	0.000 00
S(1)	−0.084 8(1)	0.001 1(3)	−0.437 2(2)
N(1)	−0.041 7(2)	−0.003 0(6)	−0.193 8(4)
C(01)	−0.060 0(3)	−0.003 0(7)	−0.293 6(5)
P(1)	0.117 41(9)	0.182 6(2)	0.031 4(2)
P(2)	−0.114 91(9)	−0.176 2(2)	−0.010 6(2)
O(1)	−0.072 5(2)	−0.109 7(3)	−0.026 7(4)
O(2)	0.064 5(2)	0.116 7(3)	0.013 7(4)
O(3)	−0.183 1(2)	−0.199 1(4)	−0.130 3(4)
O(4)	0.112 4(2)	0.289 8(3)	0.069 1(4)
C(11)	0.145 7(4)	0.284 1(6)	−0.123 2(7)
C(12)	0.143 6(5)	0.295 2(8)	−0.232 8(10)
C(13)	0.106 8(4)	0.231 3(8)	−0.325 3(8)
C(14)	0.075 9(4)	0.157 1(7)	−0.309 1(7)
C(15)	0.079 2(3)	0.142 3(6)	−0.203 0(7)
C(16)	0.114 6(3)	0.209 0(5)	−0.108 4(6)
C(21)	0.198 2(3)	0.060 8(6)	0.216 4(6)
C(22)	0.257 5(4)	0.020 9(6)	0.304 1(6)
C(23)	0.313 1(4)	0.056 0(7)	0.317 4(8)
C(24)	0.312 4(4)	0.131 4(9)	0.248 2(9)
C(25)	0.252 6(4)	0.172 4(7)	0.161 2(8)
C(26)	0.195 4(3)	0.136 1(5)	0.145 4(6)
C(31)	0.158 9(5)	0.380 8(7)	0.248 0(8)
C(32)	0.163 4(5)	0.410 1(8)	0.354 0(9)
C(33)	0.128 8(5)	0.362 2(8)	0.391 2(8)
C(34)	0.086 8(4)	0.289 7(7)	0.322 0(8)
C(35)	0.081 5(4)	0.261 6(6)	0.216 3(7)
C(36)	0.117 9(3)	0.309 7(5)	0.181 7(6)
C(41)	−0.161 4(3)	−0.192 3(5)	−0.292 6(6)
C(42)	−0.177 5(4)	−0.227 1(7)	−0.405 5(6)
C(43)	−0.222 3(5)	−0.298 4(7)	−0.462 1(7)
C(44)	−0.251 2(4)	−0.339 9(6)	−0.407 4(8)
C(45)	−0.236 6(4)	−0.308 3(6)	−0.293 7(7)
C(46)	−0.190 8(3)	−0.235 7(6)	−0.238 5(6)
C(51)	−0.008 7(3)	−0.295 1(6)	0.115 6(6)
C(52)	0.024 0(4)	−0.382 9(7)	0.159 6(8)
C(53)	−0.010 6(5)	−0.464 6(7)	0.132 7(9)
C(54)	−0.076 6(6)	−0.464 7(6)	0.065 9(10)
C(55)	−0.109 8(4)	−0.375 8(6)	0.026 0(8)
C(56)	−0.076 2(3)	−0.291 1(4)	0.048 7(5)
C(61)	−0.199 8(4)	−0.069 7(6)	0.030 9(7)
C(62)	−0.218 8(4)	−0.029 0(6)	0.103 8(8)
C(63)	−0.182 9(4)	−0.045 5(6)	0.225 4(7)
C(64)	−0.129 8(5)	−0.099 2(7)	0.272 6(7)
C(65)	−0.109 5(4)	−0.142 6(6)	0.201 7(6)
C(66)	−0.144 0(3)	−0.127 1(4)	0.079 0(5)
C(71)	0.500 00	0.255 5(13)	0.500 00
C(72)	0.476 4(5)	0.202 8(10)	0.559 1(9)
C(73)	0.481 7(7)	0.101 5(10)	0.567 7(12)
C(74)	0.500 00	0.051 5(17)	0.500 00
C(75)	0.500 00	−0.060 9(13)	0.500 00

Table 3 Selected bond lengths (Å) and angles (°) in [Mn{$OPPh_2(OPh)\}_4(NCS)_2]\cdot C_6H_5Me$

Mn–N(1)	2.173(5)	P(1)–C(16)	1.827(9)
Mn–O(1)	2.196(5)	P(1)–C(26)	1.794(6)
Mn–O(2)	2.176(5)	P(2)–O(1)	1.468(6)
S(1)–C(01)	1.640(7)	P(2)–O(3)	1.592(4)
N(1)–C(01)	1.134(8)	P(2)–C(56)	1.788(6)
P(1)–O(2)	1.483(5)	P(2)–C(66)	1.787(9)
P(1)–O(4)	1.575(5)		
O(1)–Mn–N(1)	87.8(2)	O(4)–P(1)–O(2)	114.5(3)
O(2)–Mn–N(1)	88.9(2)	O(1)–Mn–O(1^I)	93.5(3)
O(2)–Mn–O(1)	174.7(1)	P(2)–O(1)–Mn	164.5(3)
C(01)–N(1)–Mn	176.0(6)	P(1)–O(2)–Mn	169.9(3)
N(1)–C(01)–S(1)	177.7(8)	O(2)–Mn–O(2^I)	85.4(3)

Symmetry equivalent position: I $-x, y, -z$.

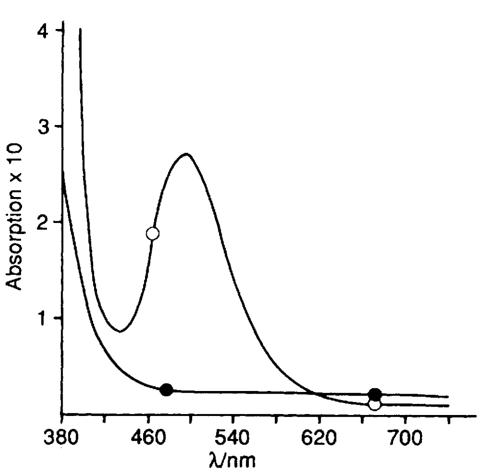

Fig. 2 Visible spectrum of a 5.21×10^{-4} mol dm^{-3} solution of [Mn{$OPPh_2(OPh)\}_4I_2$] in toluene (○), and *ca.* 7 d after exposure to SO_2 (●)

However, subsequent elemental analyses correspond only to the monoadduct, [Mn{$OPPh_2(OPh)\}_4I_2(SO_2)$] [Found (Calc.): C, 56.1 (55.8); H, 4.2 (3.9); S, 2.3 (2.1)%] and ν(SO) is not distinguishable in broad absorptions between 1250 and 1040 cm^{-1}.

Moreover, only the monoadduct can be isolated from reactions in slurries. This mirrors to a certain extent the situation with [$Mn(OPPh_3)_4I_2$], where we observed an uptake of 2 mol SO_2 per mol of complex, but where one is preferentially lost at 129 °C. It is remarkable, however, that a change in ligand from $OPPh_3$ to $OPPh_2(OPh)$ can make the loss of the more labile SO_2 so much easier in the case of the phosphinate complex; however, both complexes melt before the second SO_2 molecule is lost.

There is also another difference, for whereas the SO_2 adduct of [$Mn(OPPh_3)_4I_2$] is indefinitely stable in SO_2-saturated solvents that of [Mn{$OPPh_2(OPh)\}_4I_2$] turns red after approximately 24 h. Spectrophotometric measurements (Fig. 2) indicate that this represents the quantitative formation of I_2. In addition a black solid precipitates which, on work-up in air, yields a grey product (Found: C, 1.3; H, 0.5; Mn, 19.0; SO_4, 33.3%). X-Ray powder patterns of this solid identify the presence of $MnSO_4\cdot H_2O$. However, the microanalyses obtained clearly indicate that other inorganic products must be present in addition, but the remaining material is amorphous and cannot be identified by the X-ray powder technique. Concentration of the filtrate produces $OPPh_2(OPh)$ [Found (Calc.): C, 73.5 (73.5); H, 5.1 (5.1); P, 10.6 (10.5)%]. The overall reaction is thus of the form (2).

$$[Mn\{OPPh_2(OPh)\}_4I_2] + SO_2 \longrightarrow MnSO_4\cdot H_2O + I_2 + OPPh_2(OPh) + \text{inorganic products} \quad (2)$$

The isolation of oxidised products such as I_2 and $MnSO_4\cdot H_2O$ fails to identify the oxidant involved. The ligand $OPPh_2(OPh)$ appears to be unchanged by the reaction and, whilst aerobic oxidation cannot be ignored, rigorous attempts were made to exclude oxygen and moisture. Moreover, it must be noted that the work-up of the precipitate obtained was carried out in air, and as a result air oxidation and hydrolysis of other products to give the observed $MnSO_4\cdot H_2O$ cannot be ruled out. In addition, further inorganic products are present, which despite extensive efforts, could not be characterised. Reduced material may be present in this amorphous mixture.

Finally, a further comment on the effect of the subtle ligand change from phosphine oxide to phosphinate: radically different reactivity is observed between $[Mn(OPPh_3)_4I_2]$ and $[Mn\{OPPh_2(OPh)\}_4I_2]$, whilst $[Mn(OPPh_3)_4(NCS)_2]$ coordinates and activates SO_2 whereas $[Mn\{OPPh_2(OPh)\}_4(NCS)_2]$ is inert. Since these complexes are isostructural with sterically similar ligands, it is clear that the electronic effect on the manganese atom on changing from the phosphine oxide to phosphinate ligand must be profound. Such effects are presently difficult to rationalise. However, they are in accord with the very different behaviour of manganese(II) complexes of $OPPh_3$ and $OAsPh_3$ towards SO_2. In addition, we have also noted that trialkylphosphine oxide and tritolylphosphine oxide ligands significantly alter the reactivity of manganese(II) and cobalt(II) complexes, respectively, with sulfur dioxide.[26,27] We hope that the underlying influences of these ligands will become apparent during our systematic studies of their first-row transition-metal complexes and their reactivity with sulfur dioxide.

Experimental

Preparation of Phenyl Diphenylphosphinate.—Triethylamine ($13.2\ cm^3$, 9.5 mmol) and phenol (8.9 g, 9.5 mmol) were placed in a dry-nitrogen-filled three-necked round-bottomed flask ($500\ cm^3$), fitted with a reflux condenser and dropping funnel. Dry diethyl ether (*ca.* $200\ cm^3$) was added, after which a $Ph_2P(O)Cl$ solution (20.0 g, 8.5 mmol) in diethyl ether ($50\ cm^3$) was added dropwise over 1 h. The resultant slurry was refluxed for 1 h and filtered to remove $[NHEt_3]Cl$. The solution was then concentrated to yield $OPPh_2(OPh)$ which was recrystallised from toluene–ethanol (50:50). Yield 1.6 g (65%) [Found (Calc.): C, 73.2 (73.5); H, 5.0 (5.1)%], m.p. 133–135 °C.[28]

Preparation of Complexes.—All compounds were prepared under nitrogen using dry distilled toluene (Na, benzophenone), diethyl ether (CaH_2) or hexane (Ca). Anhydrous manganese(II) salts were prepared by thermal dehydration of the corresponding aqua salts until Karl–Fisher analyses of $<0.3\%$ were achieved.

The synthesis of $[Mn\{OPPh_2(OPh)\}_2Cl_2]$ is typical, and was performed in a predried round-bottomed flask fitted with a side-arm and ground-glass tap. Manganese dichloride (0.125 g, 0.99 mmol) was added to the flask against a flow of nitrogen. The flask was then evacuated, flame dried, and refilled with nitrogen. On cooling the procedure was repeated (with the omission of flame drying) to add $OPPh_2(OPh)$ (0.584 g; 1.98 mmol) and freshly distilled toluene ($50\ cm^3$). Finally, the flask was filled with nitrogen, sealed, and stirred for *ca.* 7 d. During this time the pink slurry of $MnCl_2$ gave way to that of white $[Mn\{OPPh_2(OPh)\}_2Cl_2]$. The solid was isolated by standard Schlenk techniques and dried *in vacuo*.

Reactions with Sulfur Dioxide.—(*i*) *Solid state.* Uptake of SO_2 was determined by the mass change of a solid sample of the complex contained in a small Rotaflo tube. Initial weighings were made under nitrogen which was then replaced by an atmosphere of sulfur dioxide. Further SO_2 was added daily to maintain a pressure of 1 atm within the tube until a constant mass was obtained. The uptake attributed to the complex was determined as the total mass increase minus a correction for the relative masses of nitrogen and sulfur dioxide occupying the tube.

(*ii*) *Toluene slurries and solutions.* Exposure to sulfur dioxide was achieved using the same techniques and equipment employed in the synthesis of the complexes; *ca.* 0.5 g samples were used to produce toluene slurries. After addition of the complex and solvent the vessel was evacuated and the vacuum let down with sulfur dioxide. Further sulfur dioxide was added until the solvent was saturated and the pressure within the flask reached 1 atm. The flask was then sealed and the contents again stirred for *ca.* 7 d, after which the products were isolated by standard Schlenk techniques and dried in a stream of nitrogen. Solutions of $[Mn\{OPPh_2(OPh)\}_4I_2]$ were similarly prepared using a known mass of complex and volume of solvent to give $10^{-4}\ mol\ dm^{-3}$ concentrations. Samples were removed for spectroscopic analysis in an argon-filled glove-box and transferred to 1 cm silica cells fitted with poly(tetrafluoroethylene) seals.

Elemental analyses were performed by the microanalytical service of the University of Manchester Institute of Science and Technology. Attempts to manipulate analytical samples of $[Mn\{OPPh_2(OPh)\}_4I_2]$ without the loss of labile SO_2 proved impossible, whilst the small quantities of SO_2 involved (*ca.* 0.5 mmol) would be difficult to detect accurately. Infrared spectra were recorded for Nujol mulls on KBr plates over a 4000–$200\ cm^{-1}$ range on a Perkin-Elmer 598 spectrophotometer, visible spectra using a Varian Cary 210 spectrophotometer. X-Ray powder patterns were recorded on a Scintag 2000 powder diffractometer using Cu-Kα radiation ($\lambda = 1.5418$ Å) in the range $2\theta = 5–70°$. Magnetic susceptibilities were recorded at 293 K using an Oxford Instruments Faraday balance, and corrected for diamagnetism using Pascal's constants.

X-Ray Structure Determination.—Crystallographic measurements were made on a Nicolet R3m/V diffractometer, operating in the ω–2θ scan mode with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\ 69$ Å).

Crystal data for $[Mn\{OPPh_2(OPh)\}_4(NCS)_2]\cdot C_6H_5Me$. $C_{81}H_{68}P_4MnN_2O_8S_2$, $M = 1440.39$, monoclinic, space group $C2$, $a = 24.214(4)$, $b = 13.712(2)$, $c = 13.059(2)$ Å, $\beta = 121.91(2)°$, $U = 3680.2$ Å^3, $Z = 2$, $D_c = 1.300\ kg\ m^{-3}$, $F(000) = 1494.0$, μ(Mo-Kα) $= 1.76\ cm^{-1}$, $T = 233$ K.

3178 Reflections were measured of which 2915 were independent with $F_o > 3\sigma(F_o)$. Heavy-atom techniques were employed to solve the structure followed by blocked-matrix least-squares refinement using SHELX 76.[29] All non-hydrogen atoms were treated anisotropically; 22 of the 35 hydrogen atoms were located from Fourier difference maps with the remainder being placed in chemically reasonable positions. Final residuals $R = 0.0524$ and $R' = 0.0506$ were attained $\{w = 1.1961/[\sigma^2(F_o) + 0.000\ 713F_o^2]\}$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

S. M. G. and D. G. K. are grateful to the SERC for the award of a Research Studentship.

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Received 7th February 1992; *Paper* 2/00671E