The Co-ordination of Small Molecules by Manganese(II) Phosphine Complexes. Part 8.[1] Irreversible Oxidation of Trimethylphosphinemanganese(II) Dihalides, $[MnX_2(PMe_3)]$ (X = Cl, Br, or I), to Bis(trimethylphosphine)manganese(III) Trihalides, $[MnX_3(PMe_3)_2]$. *X*-Ray Crystal Structure† of *trans*-Tri-iodobis-(trimethylphosphine)manganese(III), the First Example of a Trigonal-bipyramidal Manganese(III) Tertiary Phosphine Complex

Brian Beagley, Charles A. McAuliffe,* Karl Minten, and Robin G. Pritchard
Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Unlike previously reported complexes $[MnX_2(PR_3)]$ (R = alkyl, but not Me) which reversibly bind molecular oxygen, $[MnX_2(PMe_3)]$ (X = Cl, Br, or I) react irreversibly with dioxygen either in the solid state or in diethyl ether to give products from which can be sublimed $[MnX_3(PMe_3)_2]$ (after sublimation only inorganic products remain). An *X*-ray crystal-structure determination of $[MnI_3(PMe_3)_2]$ reveals a trigonal-bipyramidal geometry with three equatorial I atoms and two axial P atoms [Mn–I, 2.605(6)—2.635(3) Å; Mn–P, 2.43(1)—2.44(1) Å].

We have previously reported on the ability of some manganese(II) phosphine complexes, $[MnX_2(PR_3)]$, to co-ordinate molecular oxygen reversibly [equation (1)] and have observed

$$[MnX_2(PR_3)] + O_2 \rightleftharpoons [MnX_2(PR_3)(O_2)] \qquad (1)$$

trends in the p_{50} values[2–5] which can be related to the nature of the phosphine and the halogen. Thus, in solution the ability to bind dioxygen is generally in the order Cl > Br > I and $PR_3 > PPhR_2 > PPh_2R \gg PPh_3$ (no ability); even under high pressures $[MnX_2(PPh_3)]$ do not bind dioxygen. The trialkylphosphine complexes represent the other extreme, where binding of dioxygen is strongest, and not always reversible. Within this group the trimethylphosphine complexes are extraordinary because they react irreversibly with dioxygen to produce manganese(III) species and other products. Hill and co-workers[6] have studied the reaction between manganese(II) bromide and trimethylphosphine on thin films and, whilst the complex formed has not been characterised, they also observed irreversible oxidation of the manganese(II) to manganese(III) and the production of phosphine oxide.

We report here the synthesis and fuller details of $[MnX_2(PMe_3)]$ (X = Cl, Br, or I) and the synthesis of $[MnX_2(PMe_3)_2]$ *via* the reaction of $[MnX_2(PMe_3)]$ with dioxygen in the solid state and in solution in dry diethyl ether. We also report the *X*-ray crystal structure of *trans*-tri-iodobis(trimethylphosphine)-manganese(III), *trans*-$[MnI_3(PMe_3)_2]$, the first example of a trigonal-bipyramidal manganese(III) tertiary phosphine complex. A preliminary account of this work has been published.[7]

Results and Discussion

(a) *Solid State.*—The complexes $[MnX_2(PMe_3)]$ (X = Cl, Br, or I), Table 1, were prepared by stirring the anhydrous manganese(II) salt in a toluene–dichloromethane solvent mixture with an equimolar amount of trimethylphosphine. After removal of the solvents under vacuum the solid complexes were obtained. (Had co-ordination of the ligand not occurred then the product would have contained the PMe_3 oil.) From a steric point of view[8] the trimethylphosphine ligand is substantially smaller than, say, the triethylphosphine and we and others[9] have obtained a bis-phosphine complex with the latter, $[MnI_2(PEt_3)_2]$. Moreover, with trimethylphosphine Wilkinson and co-workers[10] have crystallographically characterised $[Mn(CH_2CMe_2Ph)_2(PMe_3)_2]$. Nevertheless, even employing a 3:1 ligand:metal salt ratio, only the complexes $[MnX_2(PMe_3)]$ were obtained after washing with toluene. Thus trimethylphosphine is an unusual ligand in not being able to form a bis-adduct with manganese(II) halides; at least not by employing our preparative method.

All the $[MnX_2(PMe_3)]$ complexes exhibit room-temperature magnetic moments, Table 2, indicative of five unpaired electrons, albeit somewhat reduced from the expected spin-only value, the reduction in magnetic moment being in the order Cl > Br > I. This probably occurs because of X–Mn–X bridges, and indeed $\nu(Mn–X)_{br}$ vibrations are observed in the Nujol-mull i.r. spectra of the chloro and bromo complexes.[11] There is no evidence whatsoever for $P(O)Me_3$; absorptions are present only for PMe_3, and a weak band is present assignable to $\nu(Mn–P)$ in each case, Table 2.

Upon exposure to dry dioxygen at room temperature the colourless solids rapidly become highly coloured, Figure 1. However, the colours produced were different to those of, for example, the closely related complexes $[MnX_2(PPhMe_2)(O_2)]$. For instance, $[MnCl_2(PPhMe_2)(O_2)]$ is purple, whereas exposure of $[MnCl_2(PMe_3)]$ to dioxygen produces a deep crimson-red solid.

The second and major difference between these '$MnX_2(PMe_3) + O_2$' materials and all other $[MnX_2(PR_3)(O_2)]$ complexes we have experienced is that, upon application of a vacuum, inert gas flow and/or heat this colour change is not reversible, even after weeks of vacuum/heat treatment. This was investigated further: samples of $[MnX_2(PMe_3)]$ were allowed to stand under dry dioxygen for two weeks and their diffuse-reflectance spectra recorded, Figure 1. These were substantially different to the diffuse-reflectance spectra of, for example, the complexes $[MnX_2(PPhMe_3)(O_2)]$,[12] and are not inconsistent with the presence of manganese(III) species.[13] The reflectance spectra are identical to those of the analysed complexes $[MnX_3(PMe_3)_2]$, Table 2 (see below).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Analytical data for the manganese(II) and manganese(III) complexes

		Analysis* (%)				
Complex	Colour	C	H	X	P	Mn
[$MnCl_2(PMe_3)$]	White	17.4 (17.8)	4.1 (4.4)	34.9 (35.1)	15.4 (15.3)	27.4 (27.2)
[$MnBr_2(PMe_3)$]	White	12.7 (12.4)	3.6 (3.1)	54.4 (55.0)	10.4 (10.7)	19.6 (18.9)
[$MnI_2(PMe_3)$]	Pale orange	9.0 (9.4)	2.5 (2.4)	66.0 (66.0)	8.1 (8.0)	14.5 (14.3)
[$MnCl_3(PMe_3)_2$]	Crimson-red	23.3 (23.0)	5.9 (5.8)	33.7 (33.9)	19.9 (19.8)	17.4 (17.5)
[$MnBr_3(PMe_3)_2$]	Purple	16.2 (16.1)	4.4 (4.1)	53.5 (53.7)	13.9 (13.9)	12.9 (12.3)
[$MnI_3(PMe_3)_2$]	Dark green	12.1 (12.3)	3.4 (3.1)	66.0 (64.8)	10.4 (10.5)	9.5 (9.3)

* Calculated values given in parentheses.

Table 2. Magnetic, i.r.,* and visible spectral data

Complex	$\mu_{eff.}$	ν(Mn–P)/cm^{-1}	ν(Mn–X)$_t$/cm^{-1}	ν(Mn–X)$_{br}$/cm^{-1}	λ/nm
[$MnCl_2(PMe_3)$]	5.8	420m		232m	
[$MnBr_2(PMe_3)$]	5.6	440m		195m	
[$MnI_2(PMe_3)$]	5.4	445w			
[$MnCl_3(PMe_3)_2$]	4.8	425m	324m		300, 385, 485, 585
[$MnBr_3(PMe_3)_2$]	4.7	445m	229m		214, 251, 410, 545, 585
[$MnI_3(PMe_3)_2$]	4.8	445w	192m		285, 386, 459, 560

* m = Medium, w = weak.

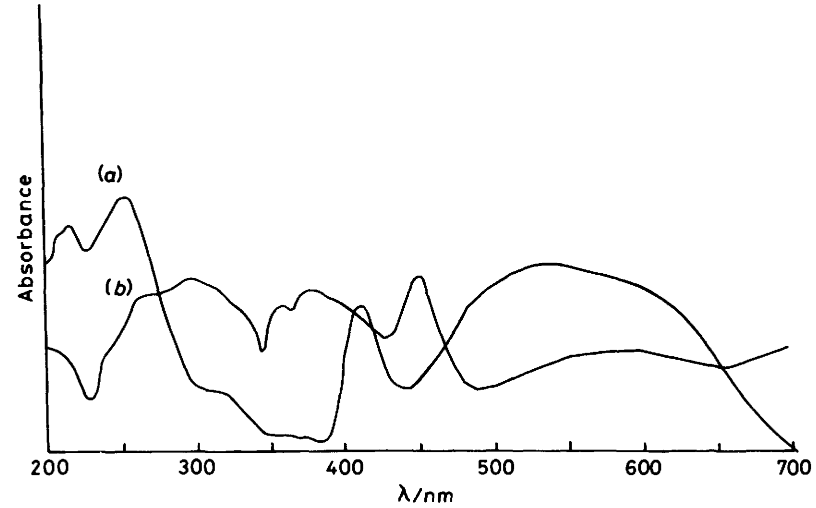

Figure 1. Electronic reflectance spectra of '$MnX_2(PMe_3) + O_2$': X = Br (*a*) or I (*b*)

Moreover [$MnX_2(PMe_3)$] exhibit a simple, broad e.s.r. signal at $g = 2$. Upon exposure to dry dioxygen the e.s.r. spectra of these samples were recorded at various times over a period of some weeks. The intensity of the broad $g = 2$ signal decreased; however, even after two weeks it did not fall to zero. These data are consistent with the production of an e.s.r. 'silent' species and an e.s.r. 'active' species.

The Nujol-mull i.r. spectra of these highly coloured materials showed the presence of co-ordinated PMe_3, but no evidence for $P(O)Me_3$. Moreover, bands assignable to ν(Mn–X)$_{br}$ disappeared, to be replaced by bands due to terminal ν(Mn–X), Table 2.

We thus suspected that exposure of [$MnX_2(PMe_3)$] to dioxygen may have produced more than one compound. The highly coloured component could be separated by vacuum sublimation, and thus [$MnX_3(PMe_3)_2$] sublimed onto the cold finger to leave a flesh-coloured solid. This latter solid contains no organic material [typical analysis: P, 0.0; H, 3.4; Mn, 9.3; I, 60.2% (O, by difference, 27.1%)], and may be a complex mixture of manganese halides; the empirical formula corresponds to $(MnI_2)_{0.2}(MnI_3)_{0.8}\cdot 10H_2O$, all the oxygen being required by the hydrogen.*

The i.r. spectrum of [$MnI_3(PMe_3)_2$] exhibits bands assignable to co-ordinated PMe_3 [no bands are present for $P(O)Me_3$] and a single ν(Mn–I) band at 192 cm^{-1} [no evidence for ν(Mn–I)$_{br}$]. This compound exhibits no e.s.r. spectrum and the room-temperature magnetic moment, $\mu_{eff.} = 4.8$, is consistent with a high-spin d^4 manganese(III) complex.

[$MnI_3(PMe_3)_2$] is highly soluble in diethyl ether, and crystals could be grown from this solvent for an *X*-ray investigation.

Crystal structure of trans-[$MnI_3(PMe_3)_2$]. Characterisation of [$MnI_3(PMe_3)_2$] revealed a packing of individual molecules in which Mn is surrounded in a trigonal-bipyramidal arrange-

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* We are grateful to a referee for helpful comments regarding the formula of this solid.

ment by three equatorial I atoms and two axial P atoms (Figure 2). The absence of halogen-bridged Mn atoms contrasts with the crystallisation behaviour of $[MnI_2(PPhMe_2)]$,[14] in which all the I atoms are in Mn–I–Mn bridges yet the *average* Mn co-ordination is also five. The unusual nature of the trigonal-bipyramidal structure of $[MnI_3(PMe_3)_2]$ is emphasised by the fact that $[MnI_2(PPhMe_2)]$ avoids five-co-ordination by having alternate Mn atoms tetrahedrally (MnI_4) and octahedrally (MnI_4P_2) co-ordinated, with the Mn–I–Mn bridged chains extending through the crystal. Co-ordinatively deficient molecules often, at least, form dimers, *e.g.* $[\{Mn(CH_2R)_2(PMe_3)\}_2]$ (R = $SiMe_3$, Bu^t, or Ph).[10] However, in $[MnI_3(PMe_3)_2]$, the Mn–I and P–C bonds are observed to be neatly staggered, which contributes to the stability of the molecule, and the bulkiness of the five ligands must hinder the increase in Mn co-ordination. The significance of the staggering is emphasised by the crystallographic mirror symmetry adopted by the molecule; each PMe_3 group has one P–C bond in the mirror plane, along with the Mn–I bond *anti* to both (Figure 2).

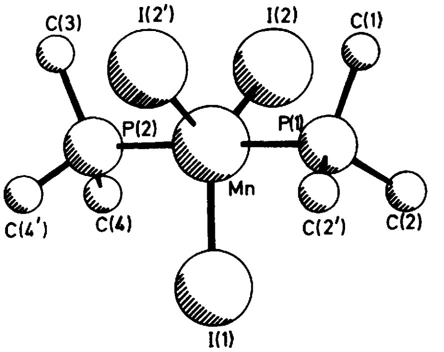

Figure 2. Molecular geometry of $[MnI_3(PMe_3)_2]$ showing the atom-labelling scheme used (hydrogen atoms were not included in refinement)

Table 3. Interatomic distances (Å) and angles (°) for $[MnI_3(PMe_3)_2]$, with estimated standard deviation in parentheses*

Mn–I(1)	2.605(6)	P(1)–C(1)	1.81(5)
Mn–I(2)	2.635(3)	P(1)–C(2)	1.89(3)
Mn–P(1)	2.43(1)	P(2)–C(3)	1.86(5)
Mn–P(2)	2.44(1)	P(2)–C(4)	1.78(3)
I(1)–Mn–I(2)	121.3(1)	Mn–P(1)–C(2)	112(1)
I(2)–Mn–I(2′)	117.5(1)	C(1)–P(1)–C(2)	106(1)
I(1)–Mn–P(1)	89.1(3)	C(2)–P(1)–C(2′)	110(2)
I(1)–Mn–P(2)	89.4(3)	Mn–P(2)–C(3)	113(2)
I(2)–Mn–P(1)	90.3(2)	Mn–P(2)–C(4)	111(1)
I(2)–Mn–P(2)	90.5(2)	C(3)–P(2)–C(4)	107(2)
Mn–P(1)–C(1)	112(1)	C(4)–P(2)–C(4′)	107(2)

* Primes denote an atom generated by the mirror plane $x, \frac{1}{2} - y, z$.

The Mn–P bonds are very short; at 2.43(1)—2.44(1) Å (Table 3) they are more than 0.2 Å shorter than the axial Mn–P bonds (in octahedral co-ordination) found in $[MnI_2(PPhMe_2)]$ (2.65—2.68 Å).[7]

The packing of the $[MnI_3(PMe_3)_2]$ molecules in the *Pnma* unit cell (Figure 3) shows the I atoms well removed from Mn atoms of neighbouring molecules. The closest intermolecular Mn···I distance is 6.21(1) Å for Mn(1)···I(1′), where the prime denotes an atom generated by the symmetry operation $1 - x, -y, -z$.

(b) *Studies in Solution*.—Our initial studies in solution were merely to observe if the electronic spectra of $[MnI_3(PMe_3)_2]$ in tetrahydrofuran (thf), toluene or diethyl ether were similar to the spectra of $[MnI_2(PMe_3)]$ in these solvents after exposure to dioxygen.

In each of these solvents $[MnI_3(PMe_3)_2]$ dissolves to give a very deep green colour and the electronic spectra (Table 4, Figure 4) are very similar to the solid-state reflectance spectrum (Figure 1) in band shape and energy. None of these solutions exhibited an e.s.r. signal, even to the limits of the detection of the instrument, pointing strongly to the presence of a d^4 species in solution. The electronic spectra of '$MnI_2(PMe_3) + O_2$' are identical in energy and profile to those of $[MnI_3(PMe_3)_2]$, but absorption coefficients of the former bands are approximately 50% of the bands in the spectra of the latter. Moreover, in both thf and diethyl ether a weak e.s.r. signal at $g = 6$ is present in the e.s.r. spectra of solutions of the former indicating that, as in the solid state, after exposure to dioxygen, $[MnI_2(PMe_3)]$ does produce some e.s.r.-active manganese(II) material in addition to $[MnI_3(PMe_3)_2]$.

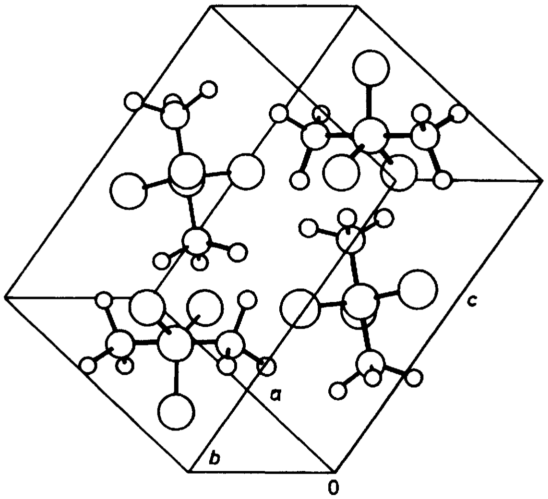

Figure 3. Packing diagram of $[MnI_3(PMe_3)_2]$ in the unit cell

Table 4. Electronic spectral data for $[MnX_3(PMe_3)_2]$ and $[MnX_2(PEt_3)(O_2)]$ in toluene

Complex	Colour of solution	λ_1/nm	λ_2/nm	$\varepsilon_{max.}$^{a}/dm^3 mol^{-1} cm^{-1}
$[MnCl_3(PMe_3)_2]$	Crimson-red	485.5*	388	183 200
$[MnBr_3(PMe_3)_2]$	Purple	514*	406.5	146 600
$[MnI_3(PMe_3)]$	Dark green	687, 585*	452, 360.5	80 200
$[MnCl_2(PEt_3)(O_2)]$	Purple	535*	401	2 600
$[MnBr_2(PEt_3)(O_2)]$	Blue	574.5*	419.5	25 600
$[MnI_2(PEt_3)(O_2)]$	Green	625,* 458	412	25 750

^{a} $\varepsilon_{max.}$ for λ_1 band (*).

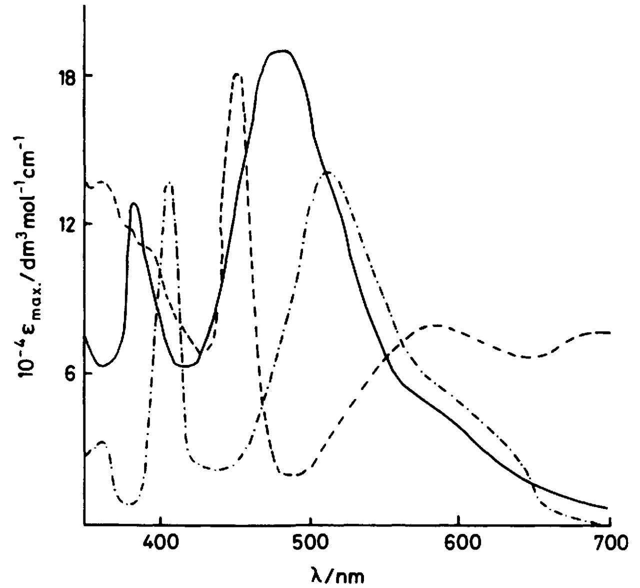

Figure 4. Electronic spectra of $[MnX_3(PMe_3)_2]$ in toluene solution at 20 °C: X = Cl (——), Br (—•—), or I (- - -)

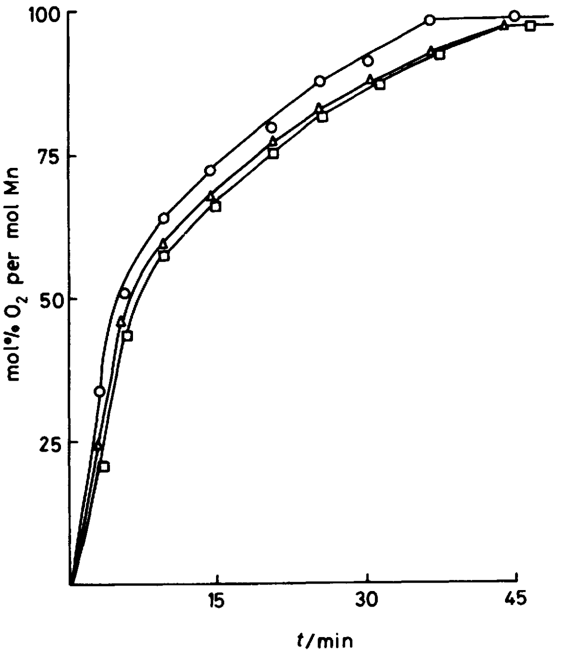

Figure 5. Dioxygen absorption of $[MnX_2(PMe_3)]$ in thf solution at −69 °C: X = Cl (○), Br (△), or I (□)

The amount of dioxygen absorbed by thf solutions of the complexes $[MnX_2(PMe_3)]$ has been examined. At −69 °C $[MnX_2(PMe_3)]$ (1.23×10^{-2} mol complex) absorbed 1.0 mol O_2 per mol Mn after having subtracted the dioxygen absorbed by the thf solvent alone. Figure 5 shows that the complete absorption of dioxygen (a 250-cm^3 round-bottomed flask containing 100 cm^3 of the manganese solution magnetically stirred) by $[MnX_2(PMe_3)]$ takes *ca.* 40 min. Under the same conditions solutions of $[MnX_2(PEt_3)]$ take *ca.* 5—6 min to dioxygenate, *i.e.* the reaction of $[MnX_2(PEt_3)]$ to form $[MnX_2(PEt_3)(O_2)]$ is much faster than the oxygenation of $[MnX_2(PMe_3)]$ to $[MnX_3(PMe_3)_2]$.

Table 5. Fractional atomic co-ordinates ($\times 10^4$) for $[MnI_3(PMe_3)_2]$, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Mn	6 954(6)	2 500	291(3)
I(1)	5 373(3)	2 500	−1 103(2)
I(2)	7 776(2)	483(2)	1 027(1)
P(1)	5 152(12)	2 500	1 344(7)
P(2)	8 728(13)	2 500	−803(7)
C(1)	5 657(43)	2 500	2 549(31)
C(2)	4 136(28)	1 115(29)	1 195(21)
C(3)	10 306(33)	2 500(9)	−225(38)
C(4)	8 690(38)	1 219(28)	−1 535(20)

Green and co-workers[15] have concluded from experiments with manganese(II) salts, $PPhMe_2$, and dioxygen in thf that the highly coloured mixtures they generated were due to manganese(III) chromophores in the presence of phosphine oxide. We have agreed[5] that their experiments would lead to the generation of these products; similar observations were made by us[16] prior to the report by Green and co-workers.[15] In order to further dispell the notion that the reversible reaction of, for example, $[MnX_2(PEt_3)]$ complexes with dioxygen leads to irreversibly oxidised products as does the reaction of $[MnX_2(PMe_3)]$ with dioxygen, we compare these systems in Table 4. The two systems are quite different.

(c) *Conclusions.*—It is possible to isolate $[MnX_2(PMe_3)]$ complexes, of identical stoicheiometry to the reversible co-ordinators of dioxygen $[MnX_2(PR_3)]$ ($R \neq$ Me or Ph), and the two types of complex may be structurally similar. Complexes of stoicheiometry $[MnX_2(PMe_3)_2]$ could not be isolated.

Whereas, for example, $[MnX_2(PPhMe_2)]$ complexes can reversibly co-ordinate dioxygen without either the manganese(II) or the phosphine undergoing irreversible oxidation, exposure of $[MnX_2(PMe_3)]$ complexes to dioxygen in the solid state or in solution results in the irreversible absorption of dioxygen to produce, amongst other product(s), $[MnX_3(PMe_3)_2]$. No oxidation of the phosphine is observed, and this result must suggest that, since Hill and co-workers[6] observed $P(O)Me_3$ in their products then it is unlikely that the materials they produced by *in situ* preparations on thin films have either the stoicheiometry or structure of $[MnX_2(PMe_3)]$ prepared here.

For the systems $[MnX_2(PMe_3)]$ (irreversible reaction with O_2) the quantity of dioxygen absorbed is 1 mol O_2 per mol Mn, and is considerably faster for the reversible systems than for the $[MnX_2(PMe_3)]$ complexes.

A summary of our observations thus far on the [MnX$_2$(phosphine)] (X = Cl, Br, or I) complexes in their reaction with dioxygen is: (*a*) PPh_3, no reaction; (*b*) $PPh_2R < PPhR_2 < PR_3$, increasingly strong O_2-binding by Mn; (*c*) PMe_3, irreversible oxidation of Mn.

Experimental

Solvent drying, dioxygen uptake measurements, e.s.r., i.r., and visible spectra were performed or obtained as previously described.[4,17,18]

Preparation of $[MnX_3(PMe_3)_2]$ (X = Cl, Br *or* I).—Two methods of preparation are available and both will be illustrated for the case of $[MnI_3(PMe_3)_2]$.

(*a*) A pre-dried flask (50 cm^3) was charged with a pure sample of $[MnI_2(PMe_3)]$ (0.5 g) in a dry-box under dry argon. The flask was evacuated and slowly returned to atmospheric pressure under dry dioxygen. The surface turned green almost instantly, even under a trace amount of dioxygen, but, typically, complete oxidation took 5—7 d at room temperature (this was shown by monitoring the e.s.r. spectrum until it was constant). After this time the dark green powder was removed from the reaction flask to a vacuum sublimation apparatus, and sublimation achieved at 120 °C (0.1 mmHg, *ca.* 13 Pa) to give a dark green sublimate, $[MnI_3(PMe_3)_2]$, and a flesh-coloured residue. Yields of $[MnI_3(PMe_3)_2]$ were typically 45—52%.

(*b*) A pre-dried flask (50 cm^3) was charged in a dry-box under an argon atmosphere with a pure sample of $[MnI_3(PMe_3)]$ (1.1 g, 2.8 mmol). To this was added dry diethyl ether (100 cm^3), after which the solution was stirred under an atmosphere of dry dioxygen for *ca.* 1 h. The diethyl ether was then evaporated and the green powder sublimed as before. Yields were *ca.* 40%.

Preparation of $[MnX_2(PMe_3)]$ (X = Cl, Br, *or* I).—These complexes were prepared by our standard method.[18] **CAUTION**: In addition to the great care we continuously urge regarding the use of dry reagents, inert gases, and solvents, we additionally urge caution regarding the use of the pyrophoric trimethylphosphine ligand, and, since the reaction of $[MnX_2(PMe_3)]$ with dioxygen is irreversible then these compounds should be handled and stored under strictly inert conditions.

Crystallographic Study of trans-$[MnI_3(PMe_3)_2]$.—Deep green crystals suitable for *X*-ray crystallography, but not of high quality, were grown from anhydrous diethyl ether.

Crystal data. $C_6H_{18}I_3MnP_2$, $M = 587.8$, orthorhombic, space group *Pnma*, $a = 10.509(1)$, $b = 11.167(8)$, $c = 14.398(2)$ Å, $U = 1\,689.7$ Å^3, $D_c = 2.31$ g cm^{-3}, $Z = 4$, $F(000) = 1\,072$, Mo-K_α radiation (graphite monochromatised), $\lambda = 0.710\,69$ Å.

3 458 Intensities were measured in the range $0.01 < (\sin\theta)/\lambda < 0.60$ Å^{-1} on a CAD-4 diffractometer and reduced to 671 unique reflections with $F > 3\sigma(F)$ for subsequent structure determination and refinement. A Patterson map revealed the triangle of I atoms and other non-hydrogen atoms were found by Fourier methods. Refinement using SHELX[19] treated all the non-hydrogen atoms anisotropically. Hydrogen atoms were not included owing to data limitations. The final *R* value was 0.081, with 64 variables. Final fractional atomic co-ordinates are given in Table 5.

Acknowledgements

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