The Synthesis of Silica-supported Phosphine and Phosphine Oxide Complexes of Manganese(II) Iodide and their Reaction with Sulphur Dioxide *

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$MnI_2(Ph_2PCH_2CH_2{\cdot}sil)$ (sil = silica surface) can be prepared from $Ph_2PCH_2CH_2Si(OMe)_3$ either by reaction with dehydrated silica and then with anhydrous manganese(II) iodide or *vice versa*. This complex reacts rapidly with sulphur dioxide in the solid state to yield an adduct with an essentially 1 : 1 Mn : SO_2 ratio. Applying a vacuum removes a considerable amount of the sulphur dioxide and the process of addition/desorption appears to be almost indefinitely repeatable. Peracetic acid oxidation of $Ph_2PCH_2CH_2Si(OMe)_3$ gives $[Ph_2P(O)CH_2CH_2Si(O-)_3]_n$ from which $[\{MnI_2[Ph_2P(O)CH_2CH_2Si(O-)_3]_{1.5}\}_n]$ can be formed. This yellow complex rapidly becomes deep red on exposure to sulphur dioxide to form a complex with a Mn : SO_2 ratio of 1 : 0.8; however, the reaction does not appear to be reversible.

We have recently observed that manganese(II) complexes of certain phosphines and phosphine oxides can bind sulphur dioxide.[1,2] In the former case[1] irreversible uptake of sulphur dioxide is seen for $[MnX_2(PR_3)]$ to give $[MnX_2(PR_3)(SO_2)_{0.66}]$ and, moreover, the reaction is dependent on the nature of X (for X = I, all phosphine complexes active; for X = Cl, no phosphine complexes active; for X = Br, activity depends upon nature of phosphine). These observations made us seek other manganese(II) systems and we have shown[2] that the complex $[MnI_2(OPPh_3)_4]$ undergoes reaction with sulphur dioxide to give SO_2 insertion into the Mn–I bonds, *viz.* $[Mn(O_2SI)_2(OPPh_3)_4]$. This SO_2 insertion is demi-reversible, either by heating to 129 °C or by placing the complex under vacuum for 2—3 h [equation (1)].

$$[Mn(O_2SI)_2(OPPh_3)_4] \underset{+SO_2}{\overset{-SO_2}{\rightleftharpoons}} [MnI(O_2SI)(OPPh_3)_4] \quad (1)$$

There is a great deal of current interest in the binding of sulphur dioxide by transition-metal complexes,[3] arising from both academic curiosity and the fact that sulphur dioxide emissions into the atmosphere provide mankind with an insidious pollution problem. We are therefore extending our investigations into systems such as manganese(II) bound to polymeric phosphine and phosphine oxide ligands.

Results and Discussion

Ligands groups can be chemically bonded to silica by reaction of the surface silanols with molecules of the type $RSiX_2$, in which R is an organic group containing a ligand and X is a hydrolysable group.[4,5] In the experiments reported here the anchoring reaction of $Ph_2PCH_2CH_2Si(OMe)_3$ and $[MnI_2\{Ph_2PCH_2CH_2Si(OMe)_3\}]$ with dehydrated high surface area (*ca.* 300 m^2 g^{-1}) silica forms very stable Si–O–Si linkages under quite mild conditions. The final product complex $MnI_2(Ph_2PCH_2CH_2{\cdot}sil)$ (2; sil = silica surface) can be formed in two ways, see Scheme.

The bifunctional phosphine ligand $Ph_2PCH_2CH_2Si(OMe)_3$ plays an integral part in the synthesis of the silica-supported phosphine and phosphine oxides, and is itself prepared by u.v. light-induced addition of diphenylphosphine[6] to trimethoxy(vinyl)silane. The product is a colourless liquid (b.p. 160 °C/0.1 Torr) and its i.r. spectrum exhibits ν(Si–C) at 1 257 cm^{-1}; no P–H absorptions (*ca.* 2 280 cm^{-1}) are observed. Its ^1H n.m.r. spectrum exhibits signals at δ 0.5—0.8 ($-CH_2-$), 1.9—2.2 ($-CH_2-$), 3.3—3.4 (CH_3-), and 6.9—7.8 p.p.m. (aromatic), and the expected integration 2:2:9:10 is observed. The ^{31}P n.m.r. spectrum in $CDCl_3$ shows one signal at δ −11 p.p.m., and elemental analyses are in excellent agreement with the proposed formulation, Table.

Table. Analytical data for the compounds

	Analysis * (%)		
Compound	C	H	P
$Ph_2PCH_2CH_2Si(OMe)_3$	61.1	6.8	9.2
	(61.1)	(6.9)	(9.3)
(1) $[MnI_2\{Ph_2PCH_2CH_2Si(OMe)_3\}]$	31.6	4.0	4.8
	(32.0)	(3.6)	(4.9)
(3) $[Ph_2P(O)CH_2CH_2Si(O-)_3]_n$	53.2	4.9	10.3
	(55.1)	(4.6)	(10.2)
(4) $[\{MnI_2[Ph_2P(O)CH_2CH_2Si(O-)_3]_{1.5}\}_n]$	32.7	3.6	5.8
	(32.9)	(3.3)	(6.1)

* Calculated values in parentheses.

The preparation of $[MnI_2\{Ph_2PCH_2CH_2Si(OMe)_3\}]$ (1) is critically dependent on the use of anhydrous solvent, manganese(II) salt, and the conditions employed.[7] Only the 1 : 1 ligand : MnI_2 adduct was isolable, Table, even when a 2 : 1 ligand : MnI_2 ratio was employed in the synthesis.

The interpretation of the elemental analyses (C, P, and Mn) for complexes (2) indicate a formula $MnI_2[Ph_2PCH_2CH_2(SiO_2)_m]$. The analyses of (2a), for example (C, 12.3; P, 2.2; Mn, 4.2%) give an elemental ratio of 14.4 : 1 : 1, almost identical to that necessary for the proposed 1 : 1 formula. Both (2a) and (2b) can thus be written as $MnI_2(Ph_2PCH_2CH_2{\cdot}sil)$, although their distribution on the silica surface (sil) may be different.

In attempts to prepare phosphine oxide ligands we have employed dioxygen and dinitrogen tetraoxide[8] to oxidise $Ph_2PCH_2CH_2Si(OMe)_3$ to $Ph_2P(O)CH_2CH_2Si(OMe)_3$. These attempts were not successful. When using peracetic acid[9] the phosphine was formed but the $-Si(OMe)_3$ group hydrolysed and subsequently polymerised. The oxidised product, (3), exhibits ν(P=O) at 1 120 cm^{-1} and its ^{31}P n.m.r. spectrum in $CDCl_3$ exhibits a singlet at δ 32.4 p.p.m. The ^1H n.m.r. spectrum exhibits signals at 0.5—1.2 ($-CH_2-$), 1.9—2.6 ($-CH_2-$), and 7.8—8.1 p.p.m. (aromatic), and there are no signals assignable to methyl or hydroxy group. The ^1H n.m.r. integration (1 : 1 : 5)

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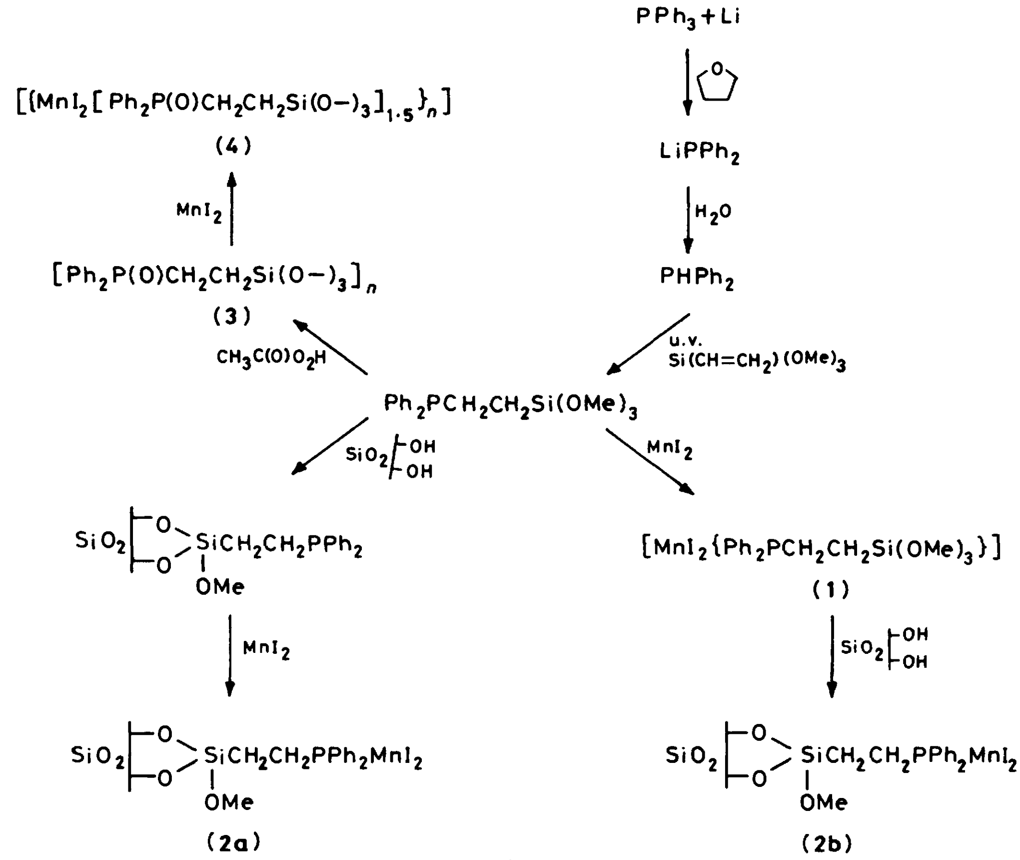
* *Non-S.I. units employed:* Torr ≈ 133 Pa, G = 10^{-4} T.



Scheme.

is consistent with the polymeric formulation $[Ph_2P(O)CH_2CH_2Si(O-)_3]_n$, as are the elemental analyses, Table. Compound (**3**) reacts with MnI_2 in a 1 : 2 ratio to yield a complex of unusual stoicheiometry, $[\{MnI_2[Ph_2P(O)CH_2CH_2Si(O-)_3]_{1.5}\}_n]$ (**4**) (Table).

Reactions with Sulphur Dioxide.—Complexes $MnI_2(Ph_2PCH_2CH_2$-sil) (**2**) react rapidly with sulphur dioxide in the solid state. For example, (**2a**) is an off-white solid but, on exposure to sulphur dioxide it rapidly becomes deep yellow. After 20 min exposure to SO_2 elemental analysis gives $S = 2.6\%$, *i.e.* there is a 1 : 1.06 Mn : SO_2 interaction. Upon application of a vacuum the yellow colour is rapidly lost and what appears to be the original off-white colour returns. The procedure appears to be repeatable almost indefinitely. However, not all the SO_2 is desorbed upon application of a vacuum. After many cycles (*ca.* 15) a constant S analysis of *ca.* 1.0% is common for all samples examined.

In contrast to (**2**) complexes (**1**) and (**4**) do not reversibly bind SO_2. Complex (**4**) is a yellow powder which, when exposed to SO_2, rapidly becomes deep red. After 20 min exposure to SO_2 elemental analysis indicates an almost 1 : 1 Mn : SO_2 uptake [Found: C, 28.7; H, 2.9; P, 5.0; S, 4.1. Calc. for (**4**) + SO_2: C, 25.0; H, 2.1; P, 4.6; S, 4.8%; *i.e.* a Mn : SO_2 ratio of 1 : 0.85]. However, several hours of applied vacuum at room temperature gave no reduction in the intensity of the red colour and almost unchanged elemental analyses (Found: C, 28.2; H, 2.7; P, 5.1; S, 3.9%).

Experimental

Diphenylphosphine was prepared by the method of Bianco and Doronzo[10] and (2-diphenylphosphinoethyl)trimethoxysilane by the method of Niebergall.[11]

Preparation of $[MnI_2\{Ph_2PCH_2CH_2Si(OMe)_3\}]$ (**1**).—A 250-cm^3 round-bottomed flask equipped with a side-arm was flame dried under vacuum and stored under argon. After evacuating the flask for 1 h the vacuum was released under dry argon, and powdered anhydrous manganese(II) iodide[12] (0.5 g, 1.60 mmol) added against a stream of argon. The flask was again evacuated and the vacuum released under dry argon. $Ph_2PCH_2CH_2Si(OMe)_3$ (0.50 g, 1.50 mmol) was mixed with dry n-pentane (125 cm^3) and added to the flask against a stream of argon. The reaction mixture was stirred for 7 d, filtered using Schlenk techniques, washed with dry n-pentane (2 × 50 cm^3), and dried *in vacuo*. The yield was quantitative.

Anchoring (**1**) *to Dehydrated Silica.*—The silica [Grace Davison 952, surface area (measured by Brunauer–Emmett–Teller N_2 adsorption) 281 $m^2\ g^{-1}$] was dehydrated by heating to 300 °C for 12 h and was allowed to cool in a stream of nitrogen. It was then suspended in degassed toluene which had been previously stirred with sodium hydroxide solution (0.1 cm^3 of 0.1 mol dm^{-3} solution per 100 cm^3 toluene). The mixture was stirred at 80 °C for 1 h, filtered, and washed several times with degassed toluene. Before use it was once more heated to 300 °C and cooled under a nitrogen stream.

The anchoring reaction was carried out in a round-bottomed flask (250 cm^3) equipped with a side-arm containing a tap. Complex (**1**) (3.2 g, 5.0 mmol) was suspended in dry toluene (30 cm^3) and dehydrated silica (1.7 g) added. The mixture was stirred at room temperature for 6 d, after which the powder-like quality of the support was lost to a paste-like consistency. The material was filtered using Schlenk techniques, washed with dry diethyl ether (2 × 50 cm^3), and extracted with hot benzene in a Soxhlet apparatus. The final product, (**2b**), was dried *in vacuo* at 50 °C for 4 h.

Preparation of Supported Complex $MnI_2(Ph_2PCH_2CH_2\cdot sil)$ (**2a**).—This consisted of two steps: the first step, the anchoring reaction, and the second step, complexation with manganese(II) iodide, were carried out by procedures essentially similar to that used to produce (**2b**).

Preparation of $[\{MnI_2[Ph_2(O)CH_2CH_2Si(O-)_3]_{1.5}\}_n]$ (**4**).—A solution of peracetic acid was prepared by gently warming 30% H_2O_2 (1.0 cm^3) with acetic anhydride until the two phases became homogeneous. This solution (estimated to contain 8 mmol of peracetic acid) was added to a mixture of $Ph_2PCH_2CH_2Si(OMe)_3$ (2.6 g, 7.8 mmol), dichloromethane (6.0 g), and acetic acid (4.0 g). The exothermic reaction caused the dichloromethane to boil; after cooling the mixture was stirred overnight. Diethyl ether (50 cm^3) was added to the light green solution with stirring and a white solid precipitated. This was filtered off and dried *in vacuo* to yield (2.0 g) a white powder.

Complex (**4**) was prepared from (**3**) and MnI_2 by the same method used to prepare (**1**).

Physical Measurements.—These were obtained as previously described.[12] The e.s.r. spectrum of (**4**) in the solid state at room temperature and at -170 °C show a broad single-line spectrum due to Mn with $g = 2.0178$ and linewidths of 850 and 1 025 G, respectively. Addition of SO_2 gives a narrower single-line spectrum with $g = 1.9954$ and a linewidth of 225 G. The spectrum of (**4**) + SO_2 in solution or mainly in solution in acetone is poorly resolved ($g = 2.002$, hyperfine splitting A_{av} ~ 100 G, and $g = 1.9954$, $A_{av} \sim 102$ G, respectively); however, six main lines characteristic of Mn^{2+} ($I = \frac{5}{2}$) are readily seen and the additional splitting observed is due to Mn^{2+} being in frozen solution.

Reactions with SO_2.—The complex under investigation (*ca.* 10 g) was finely ground and placed in a round-bottomed flask (50 cm^3) connected to a vacuum line. A vacuum was applied for 2 min and then dry sulphur dioxide admitted to the flask (1 atm pressure, 101 325 Pa). After 20 min reaction was assumed to be complete. Desorption was achieved by application of a vacuum for *ca.* 10 min at room temperature.

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