Journal of Organometallic Chemistry, 201 (1980) 437—446
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

STUDIES ON TETRAHYDROFURAN SOLUTIONS OF MANGANESE(II) DIHALIDES AND TERTIARY PHOSPHINES AND THEIR REACTIONS WITH DIOXYGEN

ROGER M. BROWN, RODERICK E. BULL, MALCOLM L.H. GREEN, PETER D. GREBENIK, JESUS J. MARTIN-POLO and D. MICHAEL P. MINGOS

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR (Great Britain)

(Received June 5th, 1980)

Summary

Solutions of $Mn(THF)_2Br_2$ and MnI_2 and tertiary phosphines in tetrahydrofuran at 0° C are oxidised by dioxygen or electrochemically giving deep blue-purple solutions which have identical electronic spectra. The principal band with λ_{max} at 570 nm has $\epsilon > 9000$ l cm^{-1} mol^{-1}. Tertiary phosphines have been shown to be oxidised to the corresponding tertiary phosphine oxides. No evidence was found for the reversible formation of dioxygen-manganese complexes.

It was recently reported that tetrahydrofuran solutions of tertiary phosphine complexes of manganese(II) dihalides and manganese(II) dithiocyanate, of formulation $[MnX_2PR_3]_n$ but of unknown structure, underwent reversible reaction with dioxygen thereby causing reversible uptake of dioxygen by these solutions [1,2,3,4]. In view of our interest in oxygen transfer from olefins catalysed by transition metals [5], and in the structure and bonding of dioxygen to transition metals [6] we decided to study the structure and reactions of the proposed dioxygen compounds. These studies are described below.

Chemical studies

The known well-characterised compound $Mn(THF)_2Br_2$ (I) [7] was prepared by crystallisation of anhydrous manganese(II) dibromide from tetrahydrofuran. The tetrahydrofuran had been dried by refluxing over and distillation from sodium benzophenone followed by storage over sodium-potassium alloy. Two separately prepared samples of the compound I were analysed for all constituent elements and found to be pure, within experimental error. Samples of analysed material were used for subsequent experiments.

Solutions of I were then treated with various tertiary phosphines and the

TABLE 1

QUALITATIVE OBSERVATIONS ON TERTIARY PHOSPHINE/MANGANESE HALIDE SYSTEMS

Compound	Tertiary phosphine	Solvent [a]	Colour [b]	Colour of [c] oxygenated system
$MnCl_2$	$PPhMe_2$	None	pale orange oil	purple-red
	$PPhMe_2$	toluene	pale yellow soln.	red
			pink-white	red
$Mn(THF)_2Br_2$ [d]	$PPhMe_2$	THF	pale yellow soln.	purple
			white solid	purple
	$PPhMe_2$	MeCN	pale yellow soln.	deep blue
	PMe_3	toluene	pale yellow soln.	purple
			white solid	blue
	PPh_2Me	THF	pale yellow soln.	blue
			white	blue
	P-n-Bu_3	THF	pale yellow soln.	blue [e]
				purple
			white solid	pink
MnI_2	$PPhMe_2$	toluene	pale yellow soln.	deep green
			pale brown oil	deep green
$Mn(SCN)_2$	$PPhMe_2$	toluene	colourless soln.	red
			cream solid	orange-red

[a] Solvent used for preparation, see Experimental section for details. [b] Colour of solutions in solvent used for preparation, or colour of solid obtained from the solution by removal of solvent. [c] Colour observed immediately (5 min) after exposure to pure dioxygen at 1 atm. [d] Similar observations have been found for the systems $MnBr_2/PEt_3/THF$; $MnBr_2/PEt_2(4\text{-}MeC_6H_4)/THF$ (or Et_2O); $MnBr_2$/P-n-Bu_3/MeCN. [e] Depending on the temperature.

mixtures were subjected to initial qualitative tests such as their reactions at room temperature with dioxygen. It was found that for all the tertiary phosphines investigated the solutions turned deep blue or purple when exposed to dioxygen. The deep colours were instantly destroyed by addition of traces of water. When the excess of dioxygen was removed the deep blue-purple colours faded rapidly on warming, leaving the original pale, almost colourless, solutions. Examples of these reactions for I and for MnI_2, $MnCl_2$ and $Mn(SCN)_2$ tertiary phosphine solutions are listed in Table 1. These observations are superficially consistent with a reversible uptake of dioxygen by a manganese(II) complex in solution.

When the deep blue-purple tetrahydrofuran solutions were allowed to stand at room temperature in the presence of an excess of dioxygen, they eventually lost their blue colour and became pale yellow or colourless. Solutions which had been exposed to an excess of dioxygen for periods of several hours were examined. For example, after a blue solution from I and PMe_2Ph in tetrahydrofuran had decolourised, the solvent was removed under reduced pressure, giving a pale yellow oily material. The IR spectrum of this oil was virtually identical to that of the system ($MnBr_2Me_2PhPO$), which was separately prepared from a pure and characterised sample of Me_2PhPO.

Further, a sample of I and PMe_2 (*p*-tolyl) in tetrahydrofuran was exposed to dioxygen containing 22.6% of the isotope ^{18}O. After the initial blue colour had gone the solvent was removed under reduced pressure and the resulting oil was pyrolysed under vacuum so that a colourless material sublimed into a cold finger. The mass and infrared spectra identified the sublimate as Me_2(*p*-tolyl)PO containing $Me_2(p\text{-tolyl})P^{18}O$ ($m/e = 170$, ca. 14%).

We also investigated the stability of the blue solutions formed from anhydrous manganese(II) dibromide and tertiary phosphines in toluene or light petroleum. In all cases the blue oxygenated solutions decolourised with time (usually within a few hours). The duration and intensity of the colour increased with increasing proportion of the tertiary phosphine. Also the colourations lasted longer when solutions were cooled.

We have carried out a more detailed and quantitative study of the system $Mn(THF)_2Br_2/P\text{-n-Bu}_3$ in tetrahydrofuran. Henceforth we refer to this solution

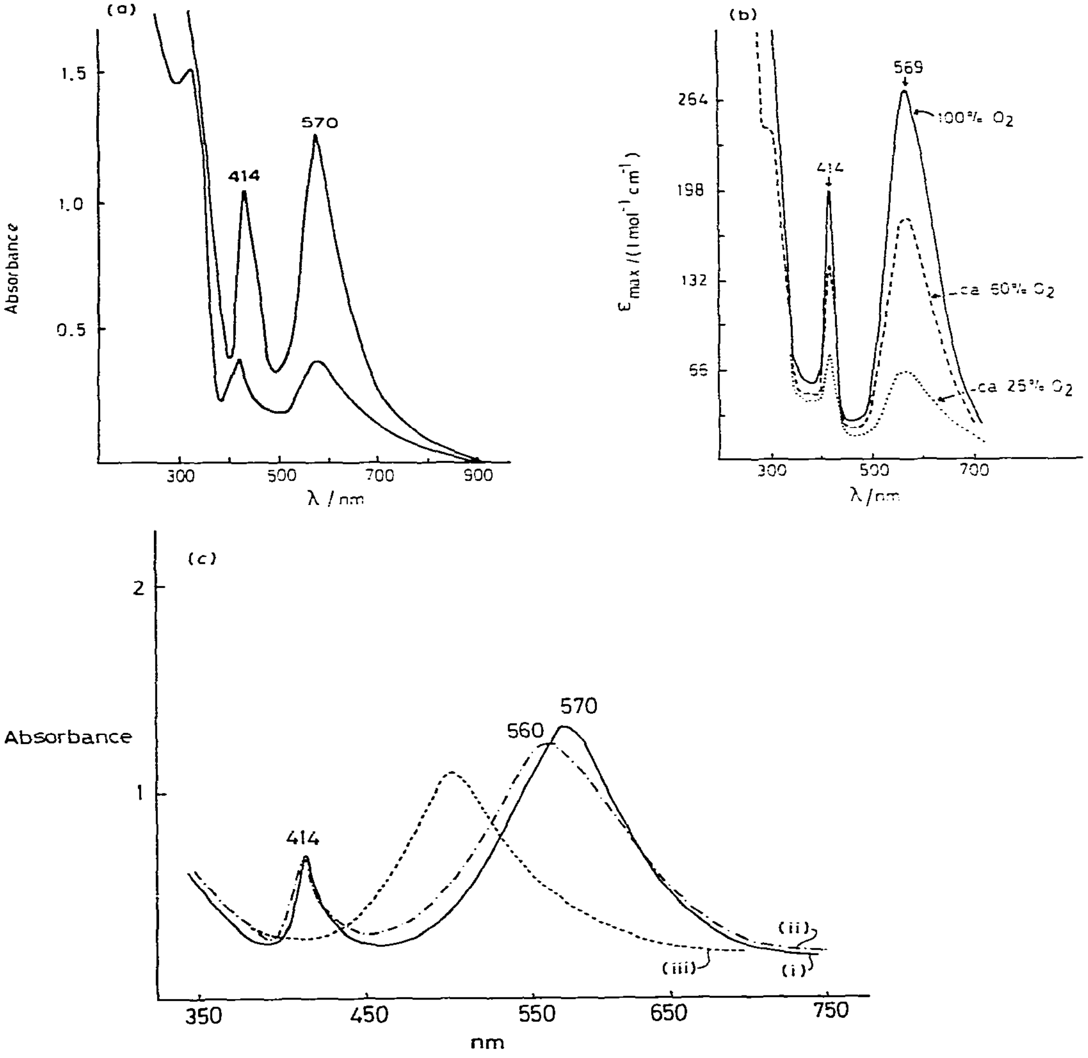
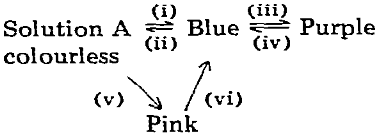


Fig. 1. (a) Electronic spectrum of the purple oxygenated solution A (or the electrochemically oxidised solution A) at 0°C and at varied concentrations. (b) The spectrum reported in ref. 1 for oxygenated solutions of $[MnBr_2P\text{-n-Bu}_3]_n$. (c) The electronic spectra of oxygenated solution A (i) at 0°C, (blue) (ii) at −60°C (purple) and (iii) spectrum obtained of the pink solution formed by addition of dioxygen to solution A at −23°C or lower.

as solution A. Reaction of solution A with dioxygen was found to give rise to several colour changes and the conditions are given in Scheme 1.

The UV visible spectrum in the region 900—190 nm of oxygenated tetrahydrofuran solutions said to contain $[MnBr_2(P\text{-n-}Bu_3)]_n$ has been reported [1]. We have investigated the spectrum of oxygenated solution A and find that the spectrum of the resulting purple solution is identical in position of the maxima and the lineshape to that described for the $[MnBr_2(P\text{-n-}Bu_3)]_n/O_2$ system, i.e. there are two bands centred at 414 nm and570 respectively (see Figure 1). Since the oxygenated solution decomposed at room temperature with loss of the blue-purple colour we built a low-temperature cell. Addition of dioxygen to solution A at —20° C gives a bright pink solution whose spectrum is shown in Figure 1. This solution seems to be stable at —20° C for prolonged periods:

SCHEME 1



Solution A is $Mn(THF)_2Br_2/P\text{-n-}Bu_3$ in THF.
(i) Add O_2 at 1 atm and 0°C gives blue solution (λ_{max} at 414 nm, 570 nm) or add $LiClO_4$ and oxidise at a platinum electrode.
(ii) Remove O_2 and warm to room temperature ($T_{1/2}$ = 15 min)
(iii) Cool to —60°C (λ_{max} at 414 nm and 560 nm (the spectrum is unaffected by the presence of lithium perchlorate).
(iv) Warm to 0°C.
(v) Add O_2 at —23°C or below (λ_{max} at 500 nm). The colour is stable at —23°C for more than 2 hours even when excess dioxygen is removed.
(vi) Warm to 0°C.

Upon warming the pink solution in the presence of dioxygen to —10° C the solution rapidly changed from pink to blue. Further warming to 0° C caused the purple solution to become blue. Cooling the solution to —20° C or below caused it to develop the more blue aspect and the resulting small changes in the electronic spectra are shown in Figure 1, details of conditions are shown in Scheme 1.

Removal of excess of dioxygen from the blue solution caused loss of colour. The rate of loss was dependent upon temperature, and below —20° C evacuated solutions retained their colour indefinitely.

It was decided to compare the solubility of dioxygen in tetrahydrofuran solutions of I (~3.0 mmol) with that in tetrahydrofuran containing I (~3.0 mmol) and tri-n-butylphosphine (~4.5 mmol) (solution A). Thus, dry tetrahydrofuran (ca. 430 cm^3) and I at —63° C (chloroform slush bath) were saturated with dioxygen at atmospheric pressure. The vessel was then attached to a Toepler pump and the dioxygen was removed from the cold deep pink tetrahydrofuran solution. An intermediate liquid dinitrogen trap prevented access of tetrahydrofuran vapour to the Toepler pump. The observed volume of dioxygen absorbed varied slightly with variation in atmospheric pressure. The volume of dioxygen absorbed by the tetrahydrofuran solutions of I was 172 ± 4 cm^3

(average). The volume of dioxygen absorbed by the corresponding solution A was 176 ± 4 cm^3. Assuming that the dioxygen would have reacted quantitatively with manganese in the molar ratio 2 Mn : O_2 then the solution A should have absorbed a further ca. 30 cm^3 of dioxygen above the value for the blank. In repeated experiments we were able to find only a small increase (ca. 4 cm^3) in uptake of dioxygen by solutions A over that by the same volume of tetrahydrofuran containing only I; although the error of these experiments is large (ca. 20%).

In another experiment a solution of pure MnI_2 in tetrahydrofuran (430 cm^3 containing 0.95 g of MnI_2) and a solution of tri-n-butylphosphine in tetrahydrofuran (0.75 cm^3) were separately saturated with dioxygen at the same (atmospheric) pressure at —63°C after fifteen minutes. The solutions were then mixed. The typical intense deep black colour developed. However, there was no further uptake of dioxygen.

The same experiment was carried out using dioxygen-saturated tetrahydrofuran solutions of I and PMe_2Ph at 0°C. On mixing the two solutions a bright-blue colour developed but there was no rapid uptake of dioxygen. After about 18 h the blue colour had disappeared and dioxygen had been absorbed. The amount of dioxygen corresponded quantitatively to half a mole of O_2 per mole of PMe_2Ph, i.e. the amount of dioxygen absorbed was sufficient to oxidise the tertiaryphosphine to the oxide Me_2PhPO, as would be expected from our previous observations. The oxide Me_2PhPO was isolated from the reaction mixture and characterised (IR).

We considered the possibility that the dioxygen caused slow oxidation of the manganese halides to a manganese(III) species which then acted as a chromophore, possibly by forming a binuclear mixed-valence charge-transfer compound. We decided to see whether the typical colours developed by addition of dioxygen to manganese halide: tertiary phosphine systems could be generated by use of other oxidants. A variable temperature 1 cm^3 UV cell was fitted with a platinum gauze electrode. Solutions of I (0.6 mmol) and $P\text{-n-}Bu_3$ (1.3 mmol) and lithium perchlorate (10^{-2} *M*) in dry tetrahydrofuran were electrochemically oxidised and immediately formed a deep blue-purple colour at the platinum anode. The UV spectrum of this purple solution was identical to that obtained by addition of dioxygen to the same solution. Also, the spectrum was identical to that shown in Figure 1 and ref. 1 for the purple species. We have also shown that the UV/vis. spectrum of the solution obtained from addition of dioxygen to I/PMe_2Ph solutions in acetonitrile was identical to that obtained by electrochemical oxidations of the same solutions containing lithium perchlorate as the supporting electrolyte. Further, electrochemical oxidation of acetonitrile solutions of $MnCl_2/PMe_2Ph$ gave a deep pink colour identical with that observed when dioxygen is added to the same solution (λ_{max} at 532 nm). We conclude that in the case cited above the blue-purple (or pink colours) are not caused by dioxygen manganese systems.

The extinction coefficient for the band centred at 569 nm in the electronic spectrum of oxygenated solutions of $MnBr_2/P\text{-n-}Bu_3$ has been reported as being 264 l mol^{-1} cm^{-1}. Since we observed that the blue colours obtained by injection of very small aliquots of dioxygen could be very intensely coloured we reinvestigated the magnitude of the extinction coefficient of the 570 nm band for the oxygenated solution A.

Three methods were used to determine the extinction coefficient, the details are given in the Experimental section. The most accurate value, obtained at —10° C to reduce the loss of intensity due to decomposition, gave a value for $\epsilon \approx 9000$ l mol^{-1} cm^{-1}. The other methods, including electrochemical oxidation, gave rather inaccurate but certainly minimal values of $\epsilon > 10^3$ l mol^{-1} cm^{-1}.

Discussion

Our studies have mainly concerned solutions of manganese(II) dibromide or diiodide in tetrahydrofuran to which tertiary phosphines were added in varying proportions. We have been unable to isolate any compounds of stoicheiometry corresponding to $[MnX_2PR_3]_n$ which have been described elsewhere [1—4]. Our attempts to prepare the compound frequently referred to as $[MnBr_2(PMe_2Ph)]_n$ led only to $Mn(THF)_2Br_2$, as discussed in the Experimental section. The electronic spectrum of oxygenated solution A is identical in appearance to that reported for oxygenated solutions of $[MnBr_2P\text{-}n\text{-}Bu_3]_n$, and therefore it seems reasonable to assume that both solutions contain the same manganese species. Also, it seems reasonable to assume that manganese(II) halide complexes with tertiary phosphine will be relatively labile.

Our studies clearly show that the solution A and related systems undergo irreversible oxidation when exposed to dioxygen, eventually giving tertiary phosphine oxides.

The initially produced deep colourations cannot be due to dioxygen-manganese complexes since the identical colours are generated by electrochemical oxidation.

A major discrepancy between our studies and previous work lies in the much larger value we find for the extinction coefficient of the bands giving rise to the colours of the oxidised species.

We can account for the reversible colourations observed when dioxygen is added or removed from our solution A, and those systems described in Table 1, by the following sequence of events:

We assume our solutions contain an equilibrium concentration of a tertiary phosphine/manganese(II) dihalide system which is slowly oxidised by dioxygen giving an intensely coloured chromophore such as a manganese(III) compound or, very possibly, there may be a binuclear mixed-valence system. This chromophore is thermally unstable at room temperature and decomposes giving manganese(II) species and either, the tertiary phosphine or solvent, both, are oxidised to the tertiary phosphine oxide and other products, respectively. Thus, in the presence of excess of dioxygen an equilibrium concentration of the chromophore is formed and when excess of dioxygen is removed then the solutions rapidly decolourise. Clearly the solutions will continue to develop the chromophore when dioxygen is added as long as there is tertiary phosphine present.

We conclude that either previous work which claims that there is reversible uptake of dioxygen by manganese(II) halide/tertiary phosphine is erroneous, or that we, being unable to make the reported compounds, are dealing with a different systems which have coincidental spectroscopic properties but different reactions towards dioxygen.

Experimental

Analyses were performed by Butterworths Ltd. Electronic spectra were recorded using a Perkin-Elmer 552 or Unicam SP800 spectrometer. Tetrahydrofuran was dried initially by refluxing over sodium-benzophenone under dinitrogen followed by distillation onto liquid sodium-potassium alloy. Immediately before use it was distilled from the alloy into the glass vessels which had been previously flamed out under vacuum. Acetonitrile was dried by refluxing over phosphorus pentoxide. $Mn(THF)_2Br_2$ was prepared as described [7] from anhydrous manganese(II) dibromide supplied by Cerac Chemical Co. Ltd. (99.5%). Manganese(II) diiodide was freshly prepared as described and was recrystallised from THF [8]. Tri-n-butylphosphine was supplied by Aldrich Chemical Co. and was vacuum distilled and its purity was monitored by ^{31}P NMR spectrum. Dimethylphenylphosphine oxide was prepared as described. Infrared spectra were measured as mulls or as thin films using Unicam SP2000 or Perkin-Elmer 457 instruments and calibrated with polystyrene.

Evidence for the formation of tertiary phosphine oxides

A solution of $Mn(THF)_2Br_2$ and PMe_2Ph in tetrahydrofuran was allowed to stand under excess of dioxygen until the initial deep blue colour had gone. The toluene was then removed from under reduced pressure leaving a pale yellow oil. The IR spectrum of the oil showed major bands at 1295m, 1285m, 1152(br)s, 1111s, 1080m, 1027w, 998w, 940s, 912m, 879m, 845m, 749s, 727s, 699m, 685w.

Anhydrous manganese(II) dibromide (0.7 g, 3.3 mmol) was suspended in dry toluene (40 cm^3) containing dimethylphenylphosphine oxide (1.2 g, 7.8 mmol). The mixture was stirred and after 3 h a pale yellow-brown oil had separated. This was washed twice with toluene and then solvent was removed in vacuo. The infrared spectrum of the oil was identical to that given above for the previous oil.

Determination of extinction coefficient

Method a. The compound $Mn(THF)_2Br_2$ (0.45 g, 1.25 mmol) was dissolved in tetrahydrofuran (15 cm^3) and tri-n-butylphosphine (54 cm^3). An aliquot (35 cm^3) of this solution was cooled to $-10°C$ in a variable temperature, silica 1 cm^3 cell and treated with measured quantities of dioxygen (0.1, 0.2 and 0.5 cm^3) at atmospheric pressure. A solid glass plunger was inserted into the body of the resulting solution through a gas-tight seal so that the oxygen was fully dissolved in the solution. After thorough mixing the electronic spectrum of the resulting deep blue solution was measured several times (at $-10°C$). The extinction coefficient was calculated on the assumption of the following stoicheiometry for the oxidised species: $O_2 + 2\,Mn^{2+} \rightleftharpoons MnO_2^{2+}$. The value (average of 3 separate experiments) was $\epsilon_{min} = 9000 \pm 540$ l cm^{-1} mol^{-1}.

Method b. A related experiment was carried out by addition of small aliquots of dioxygen to solutions of I in tetrahydrofuran containing PMe_2Ph. The apparatus used limited the experiment to room temperature and at this temperature the solutions quite rapidly decolourise. The data gave a minimum value of $\epsilon = 1240$ l cm^{-1} mol^{-1}. However, the experiment was likely to be highly inaccurate as it was assumed that all dioxygen had dissolved, although there was excess of the gas observed above the solution.

Method c. A solution of I in acetonitrile in the presence of PMe_2Ph at room temperature in a silica cell fitted with a platinum electrode was oxidised electrochemically and the number of coulombs passed through the cell was recorded. The resulting deep blue solutions quite rapidly decomposed so that the intensity of the band at 556 nm was monitored over a period of 30 min and then the value for the intensity at zero time was estimated by extrapolation. This approach gave as a minimum value $\epsilon = 2 \times 10^3$ l cm^{-1} mol^{-1} at 560 nm. Again this value is likely to be in considerable error, for example, we have not taken account of decomposition during the electrochemical oxidation and also it was assumed that all the oxidised product was in the cell although this was visibly untrue.

Studies on the solubility of dioxygen in tetrahydrofuran solutions containing $Mn(THF)_2Br_2$ and tri-n-butylphosphine

a) Tetrahydrofuran (430 cm^3 at room temperature) and I (0.96 g) in a glass vessel was saturated with dioxygen at —63° C, apart from the tetrahydrofuran solution there was a small volume of gas above the tetrahydrofuran arising from the contraction of tetrahydrofuran on cooling. The volume of dioxygen in the apparatus, corrected for NTP, was measured by pumping the dioxygen from the tetrahydrofuran (at —63° C) through a liquid dinitrogen trap, using a Toepler pump, into a gas burette. It was found that the volume of dioxygen contained in the apparatus varied from 2.8 to 3.15 mol O_2/mol of I, giving an average of 2.97 mol (172 ± 6 cm^3). The average value for the quantity of dioxygen contained in the system was 172 ± 4 cm^3 (average of 3 runs). Solutions of I and $P\text{-n-}Bu_3$ (in the ratio 1 : 1.5 mol, respectively) in tetrahydrofuran at —63°C were similarly saturated with dioxygen at atmospheric pressure. The volume of dioxygen absorbed was determined as described above. The volume of dioxygen in the apparatus containing I, $P\text{-n-}Bu_3$ in tetrahydrofuran (430 cm^3) was 3.09 mol O_2/mol of I (176 ± 6 cm^3; average of four runs). The calculated extra amount of dioxygen required by the quantities of Mn used, for example 2.85 mmole would be 1.42 mmole = 31.8 cm^3 of dioxygen, assuming the ratio Mn : O_2 of 2 : 1. Thus there is only a very slight increase, if any, in uptake of dioxygen under these conditions. Our apparatus was not calibrated in a manner which enabled us to eliminate small errors arising from changes in atmospheric pressure although these changes were monitored.

b) A solution of I (0.96 g) (or MnI_2 0.95 g) in tetrahydrofuran (430 cm^3) and a solution of $P\text{-n-}Bu_3$ (0.8 cm^3) (or 0.75 cm^3) in tetrahydrofuran (10 cm^3) were attached to the same vacuum line and saturated with dioxygen at —63° C and 1 atmosphere pressure. The system was then closed to a mercury manometer and then the solutions were mixed together. A deep pink (or purple) solution developed within a few minutes but during this time there was, within experimental error, no uptake of dioxygen. No uptake of dioxygen was observed over a further period of 30 min.

Attempts to synthesise compounds of stoicheiometry $[MnBr_2(PR_3)]_n$

It has been reported that solutions of manganese(II) dibromide in tetrahydrofuran react with tertiary phosphines, such as PMe_2Ph to give white or pale coloured compounds of stoicheiometry $[MnBr_2(PMe_2Ph)]_n$ [1—4].

We have studied, in detail, the reaction between I and PMe_2Ph in tetrahydrofuran. This system was chosen since the compound $[MnBr_2(PMe_2Ph)]_n$ has been referred to frequently.

We found that cooling solutions of I and PMe_2Ph (in varying ratios) in tetrahydrofuran gives white-pale pink crystals. If these have been washed only once with toluene and then dried in vacuo they smell strongly of the tertiary phosphine. Further, they develop a blue colouration when exposed to dioxygen. Analysis for carbon, hydrogen, manganese and bromine give values which are reasonably consistent with those expected for the compound $[MnBr_2(PMe_2Ph)]_n$: Found: C, 26.74; H, 4.46; Br, 44.57, $[C_8H_{11}Br_2MnP]_n$ calcd.: C, 27.2; H, 3.12; Br, 45.33%. However, the infrared spectrum is very similar indeed to that of the compound I. Further rigorous washing with toluene of the white-pink crystals produces a solid which has an infrared spectrum identical to that of I. We conclude that the product we obtained from solutions of I and PMe_2Ph in tetrahydrofuran was unreacted I containing a small quantity tertiary phosphine absorbed or occluded onto the surface of the crystals. The analytical data is reasonably consistent with the formulation of very slightly impure I since both I and $[MnBr_2(PMe_2Ph)]_n$ have similar percentages of these elements which they have in common. We attempted to form the compound $[MnBr_2(PMe_2Ph)]_n$ by varying the ratios of I to the tertiary phosphine and by concentration of cold as well as warm solutions. All these experiments yield only I, often as crystals of excellent appearance.

We concluded that we were unable to prepare $[MnBr_2(PMe_2Ph)]_n$ by the conditions described in or which may be reasonably inferred from the references [1,2,4]. The microanalysis data for a compound $Mn(PPhMe_2)Br_2O_2$ has been reported [1] and we note that the data also would be consistent with a formulation such as $MnBr_2(Me_2PhPO)$, which was very slightly contaminated with a deep blue compound of similar stoicheiometry.

Experimental details for Table 1. The anhydrous manganese(II) dihalides (ca. 0.2 g) and the tertiary phosphine (1 mol per mol of manganese) either pure or as a solution (ca. 5%) were mixed. The resulting solutions were treated with dioxygen, or, solvent was removed under reduced pressure giving oils or solids which were then treated with dioxygen. The solids were not purified by crystallisation, so it may be assumed that the tertiary phosphine was present either as coordinated ligand or as uncoordinated, free phosphine.

Acknowledgements

We thank the University of Mexico (UNAM) for a grant (to J.J.M.-P.) and the Science Research Council for a grant (to P.D.G.).

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