Journal of Organometallic Chemistry 228 (1982) 255—264
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. A REPLY TO A PAPER BY GREEN, MINGOS AND COWORKERS

CHARLES A. McAULIFFE

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD (Great Britain)

(Received November 16th, 1981)

Summary

Green, Mingos and co-workers have described the oxidation of tertiary phosphines by dioxygen in the presence of manganese(II) species. Their observations and some conclusions mirror quite well our own observations (colour changes, production of ν(P=O) bands) and conclusions on manganese(III)-phosphine oxide systems in published papers not cited by Green and Mingos. Their experimental observations indicate that the high-valent manganese/phosphine oxide system does not bind dioxygen, which agrees with our own observations. However, this system bears no relation to our authentic haem analogues, $Mn(PR_3)X_2$; some properties of the latter in reversibly binding dioxygen and carbon monoxide are described in this communication.

A recent publication by Brown, Bull, Green, Grebenik, Martin-Polo and Mingos, entitled "Studies on Tetrahydrofuran Solutions of Manganese(II) Dihalides and Tertiary Phosphines and their Reactions with Dioxygen" [1], purports to have some relevance to our work on the reversible coordination of molecular oxygen by the haem analogue compounds, $Mn(PR_3)X_2$ (R_3 = trialkyl, phenyldialkyl; X = Cl, Br, I, NCS) [3]. Most of our published work in this area [2,4—6] was not cited by Green, Mingos and co-workers [1]; in particular, many of their observations had previously been reported by us [2,6], but they appear to be unaware of this.

In this paper I wish to do three things: 1. Discuss a reasonable approach to the synthesis of transition metal-phosphine complexes generally, and to metal complexes which coordinate dioxygen in particular. In the case of the synthesis of $Mn(PR_3)X_2$ complexes, both of these concerns come together. 2. To discuss some aspects of the paper by Green, Mingos and co-workers [1], and 3.

to mention some aspects of our work on $Mn(PR_3)X_2$ compounds which show what interesting molecules they are proving to be.

1. Synthesis of transition metal-phosphine complexes

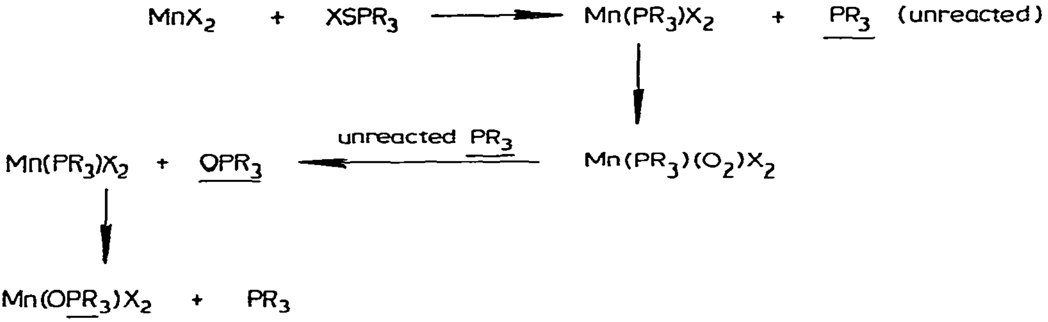
Whilst it may be possible to prepare some tertiary phosphine complexes, e.g. PPh_3 complexes, in air or dioxygen, it is not a procedure to be recommended. As is well known, phosphines are capable of oxidation to phosphine oxides in air, a process made catalytic by, for example, $M(PPh_3)_4$ (M = Pd, Pt) [7] or cobalt(II) chloride [8]. It is also true that a number of metal-phosphine complexes can bind dioxygen as an additional ligand [9—11], but it is axiomatic that these complexes, which are sensitive to dioxygen, should be synthesized in the absence of dioxygen. In view of Green and Mingos' previous involvement in metal-promoted oxygenations of organic substrates [1] we are surprised that they should approach the synthesis of $Mn(PR_3)X_2$ compounds by deliberately employing dioxygen atmospheres and saturating their solvents with dioxygen prior to reaction.

The synthesis of $Mn(PR_3)X_2$ is quite straightforward provided that attention is paid to use of anhydrous materials and conditions and the absence of dioxygen. We have repeatedly stressed this in our published work which describes our approach to Mn^{II}—ER_3 (E = P, As, Sb) syntheses [2,4—6]. All these papers were published before Green and Mingos submitted their paper for publication, but were not referred to by those authors. Reference 2, for example, states in the first sentence of the discussion: "The results described above show that all ligands (a series of phosphines) used in this study, with one exception, react with manganese(II) halides under apparently 'anhydrous' conditions to produce complexes of the corresponding oxidized ligand." Again in ref. 5, even in the Abstract, in describing the Mn^{II}—ER_3 complexes we had prepared we stated: "EPR evidence also suggests that trace amounts of moisture readily decompose these complexes . . .".

2. The paper by Green and Mingos and their coworkers [1]

We consider that there are significant differences in our own approach, developed over a number of years, and that of Green et al. to the synthesis of the $Mn(PR_3)X_2$ complexes. Absolutely crucial to the formation of a stable manganese(II)—phosphine bond is the use of absolutely anhydrous manganese(II) salts. The manganese(II) bromide (Cerac Chemical Co. Ltd.) employed by the authors [1] is, as such, in our experience not capable of forming $Mn(PR_3)Br_2$ complexes. This commercially available material typically contains between 3.8% (UMIST Microanalytical Laboratory) and 4.2% H_2O (Galbraith Laboratory, Knoxville, Tenn.). The formation of phosphine oxide complexes resulting from reaction with incompletely anhydrous manganese(II) salts was described by us in 1974 [4]. Procedures for obtaining manganese(II) salts sufficiently anhydrous for our own successful syntheses of $Mn(PR_3)X_2$ compounds have recently been published [12]. No MnX_2 salt is used in our experiments which gives a Karl Fischer H_2O analysis of $>0.1\%$. All our MnX_2 salts are stored in a dry box under argon and are assayed for H_2O at least once every two weeks. We should also point out that our most recent observations indicate that, for tetrahydrofuran, distillation from potassium benzophenone (usually 24 h reflux under pure N_2 or Ar is sufficient for the blue/purple colour to develop, indicative of dry THF) is superior to that from sodium benzophenone, although we have used the latter reagent with some success. Additionally the THF is distilled directly into predried, Ar-containing flasks and used immediately. We never store THF after distillation, even over a drying agent.

In addition to Green et al.'s direct use of commercial manganese(II) bromide, there is another fundamental error in their approach to the $Mn(PR_3)X_2$ compounds. Apart from their qualitative experiments referred to in their Table 1 in which they say they employ Mn/PR_3 ratios of 1/1 (though they do not say how long they allow for reaction prior to addition of dioxygen), in all other experiments they state that they use an excess of phosphine (sometimes a very large excess) over and above the 1/1 stoichiometry necessary for $Mn(PR_3)X_2$ formation. In view of their stated interest in oxygen transfer to olefins [1], it is surprising that they seem not to have considered (and taken steps to avoid) the oxygen transfer possibility as shown in Scheme 1.



We have a good deal of evidence that this obvious process does occur when any excess of phosphine is present. Moreover, their curious use of "excess dioxygen" in many of their experiments would ensure that the prospects for the formation and subsequent stable existence of $Mn(PR_3)X_2$ would be minimal.

It is necessary to examine the paper of Green et al. [1] in some detail in order to point out that the controversy they have generated stems essentially from serious differences between their techniques and ours. In their paper [1] Table 1 refers to studies in MeCN, despite the fact that we have stated in print: "We would stress that MeCN is a solvent to be completely avoided for investigations of $Mn^{II}PR_3$ complexes" [6]. We found [6] that in MeCN reaction of $Mn(THF)_2Br_2$ and $PPhMe_2$ in the presence of dioxygen rapidly gave $OPPhMe_2$ and a highly coloured manganese(III) species. It is no doubt this manganese(III) "chromophore" which pervades the dioxygen-saturated non-anhydrous systems of Green et al. [1]. It is well established that manganese(III) salts in ether solvents are highly coloured [13], a fact we refer to [2] in a paper not cited by Green et al. [1]. In fact our paper entitled "The reaction of manganese(III) chloride with group VB ligands" [2] specifically lists the deep green, red or blue solutions which become colourless on standing and the products, viz. manganese(III) and phosphine oxides; these are the colours Green et al. list in Table 1 of their paper

[1]. We make no claim that the manganese(III)/phosphine oxide systems reversibly bind dioxygen. They may well be highly coloured, but only Green et al. [1] relate this property to the ability of authentic $Mn(PR_3)X_2$ to bind dioxygen. On p. 2 of their paper [1, p. 438] they begin a series of descriptions of the preparation of a range of phosphine oxides and their manganese complexes. We agree with Green and Mingos that the conditions they employ lead to the production of these oxidized materials. Previous work by us shows that manganese(II) complexes of phosphine oxides and the highly coloured manganese(III)/phosphine oxide system do not reversibly bind dioxygen [2,4—6]. The contents of p. 3 and 4 of their paper [1, p. 439—440] and the Figures shown do puzzle us, for despite their experimental technique Green et al. may well have produced some $Mn(PBu^n_3)(O_2)Br_2$. However, they give little insight into how, for example, they performed their electrochemical oxidations. The manganese(II) salts they use are certainly hydrated and it would be useful to know if dioxygen is being generated in situ. However, it must be pointed out that the spectrum shown in Fig. 1(a) of the authors' paper (λ_{max} 570 nm) is claimed to be identical to the spectrum of $Mn(PBu^n_3)(O_2)Br_2$ described by us (λ_{max} 569 nm) [3]. However, in the Experimental section of their paper [1, p. 444], the authors refer to another band as occurring at 560 nm or, two lines later, at 556 nm! It would be helpful in assessing their claims of the identity of their spectrum and ours [3] if it were clear just where λ_{max} for the main band in their spectrum appeared: at 570, 560 or 556 nm. Moreover, it is very important to point out that we had published the observation that in the solvent MeCN, in which the authors carry out their electrochemical oxidations, the $Mn(PR_3)X_2$ complexes are unstable and rapidly undergo oxidation:

$$\begin{tikzcd} Mn(THF)_2Br_2 + PPhMe_2 + O_2 \arrow[r, "MeCN"] & \text{transient } Mn^{II} \arrow[dl, "\text{rapidly}"] \\ Mn^{III} + OPPhMe_2 + \text{other products} & \end{tikzcd}$$

(taken from Ref. 6)

The unstable spectrum exhibited by this system has an intense band at 575 nm and the spectrum rapidly fades [6]. This is what Green et al. observed in their electrochemical oxidations of $Mn(THF)_2Br_2 + PPhMe_2$ in MeCN [1]. They thus merely confirm what we had published (before they submitted their paper for publication), viz. that in MeCN the mixture of $Mn(THF)_2Br_2$ and $PPhMe_2$ is unstable to oxidation and gives rise to a spectrum centred around 575 nm (our value) or 556, 560, 570 nm (Green et al.). It is unfortunate that Green et al. overlooked our published work, and so inferred that the rapid oxidation of Mn^{II} to the highly coloured Mn^{III} in MeCN which they observed has a significance other than that which we discussed [6].

We note that on p. 5 of their paper [1, p. 441 lines 1—8], Green et al. quote an expected uncertainty in their quantitative measurement of dioxygen uptake which is actually greater than the expected change in volume; in view of this, it is difficult to see what that experiment could have been expected to prove. On p. 5 [1, p. 441, paragraphs 1 and 2] Green et al. describe the mixing of dioxygen-saturated THF solutions of manganese(II) species with dioxygen-saturated THF solutions of PBu^n_3 and $PPhMe_2$. Not surprisingly, they obtained phosphine oxide exactly as we should have expected. We thus agree with their conclusion [1, p. 441, paragraph 4] that their "chromophore" is probably due to a high-valent manganese species and not to a manganese dioxygen species.

We also note that on p. 443 in the 2nd paragraph of their paper, Green et al. refer to the reaction "of $Mn(THF)_2Br_2$ and $PPhMe_2$ in tetrahydrofuran", but go on to say "The toluene was then removed . . .". Was the reaction carried out in THF or toluene?

The evidence they produce on p. 443, paragraph 2 for the formation of tertiary phosphine oxides is overwhelming; indeed, as stated above, it is difficult to envisage any other major product of their reactions. We emphasize again that we have never observed reversible dioxygenation by manganese(II), -(III)-phosphine oxide complexes. However, $Mn(PR_3)X_2$ complexes do reversibly bind dioxygen [3,14—21]. In ref. 1 (p. 443, paragraph 4) Green et al. describe the reaction of $Mn(THF)_2Br_2$ with PBu^n_3 in a mole ratio we calculate to be approx. 1/170; the purpose of this escapes us, as does their calculation of extinction coefficients based on the following puzzling stoichiometry:

$$O_2 + 2\,Mn^{2+} \rightleftharpoons MnO_2{}^{2+}$$

We note that in paragraph a on p. 444 [1] Green et al. again refer to prior saturation of THF before reaction; they also, as they stated, omitted to calibrate their apparatus for dioxygen measurement. On p. 444, in paragraph (b) [1], they again describe dioxygen saturation of solutions of $Mn(THF)_2Br_2$ and PBu^n_3 prior to mixing. On p. 445 [1] Green et al. make much of the coincidence that the microanalytical data for $Mn(THF)_2Br_2$ and $Mn(PPhMe_2)Br_2$ are similar in the case of the elements they have in common, and we must thus point out that our authentic $Mn(PPhMe_2)Br_2$ [2] and many other $Mn(PR_3)X_2$ [14,15,17] complexes were analysed for every element including phosphorus, and that the compounds have the stoichiometry stated, with no phosphine oxide present.

3. The authentic $Mn(PR_3)X_2$ complexes

These complexes are readily prepared as stated, viz. by the reaction of anhydrous manganese(II) salts with tertiary phosphines in many organic solvents. This reaction must, of course, be carried out in the complete absence of dioxygen (and certainly not in the presence of "excess dioxygen" or "dioxygen saturated solutions" [1]). The method of preparation of the anhydrous salts, anhydrous solvents and the complexes has been fully described [12].

The complexes react with dioxygen either in the solid state or in solution in many organic solvents (though MeCN should be avoided [6]) to form 1/1 molecular adducts, $Mn(PR_3)(O_2)X_2$. Absorption/desorption studies of labelled $^{18}O_2$ have been published [17]. The magnetic properties of the dioxygenated complexes are most interesting. Solid state $Mn(PR_3)(O_2)X_2$ appear to contain six unpaired electrons [2,15] but in solution $S = 5/2$ [16]. No evidence for manganese(III) is observed [16].

Apart from significant changes in magnetic and vibrational spectroscopic properties which occur on oxygenation and deoxygenation, simple measurement of weight gain and loss mirror exactly what occurs in the process. For example when 4.48 g of $Mn(PPhMe_2)I_2$ (0.01 mole) is allowed to stand in an atmosphere

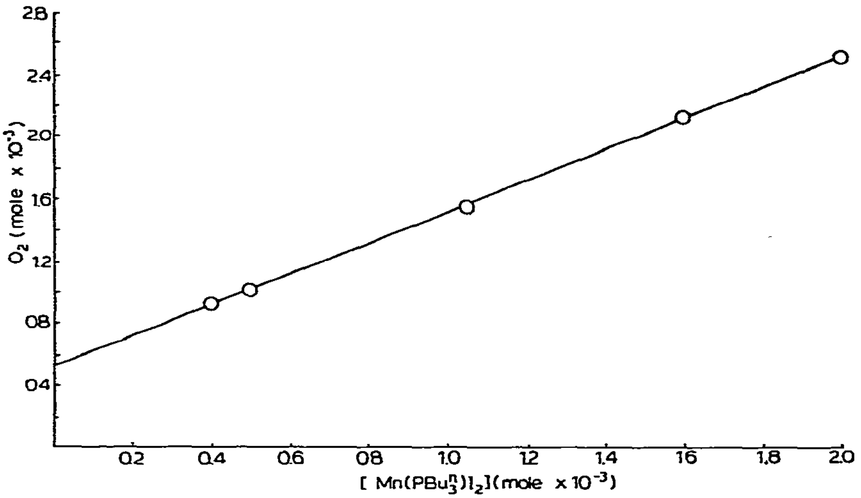


Fig. 1. Dioxygen uptake as a function of $Mn(PBu^n_3)I_2$ concentration in 100 ml THF at 0°C.

of dry dioxygen for 2 days the weight of the green $Mn(PPhMe_2)(O_2)I_2$ complex obtained is 4.80 g (0.01 mole). No further weight gain is observed over long periods. On pumping the green $Mn(PPhMe_2)(O_2)I_2$ overnight in a vacuum desiccator 4.48 g of the pale orange $Mn(PPhMe_2)I_2$ is obtained. The process is fully reversible.

Fig. 1 shows a plot of dioxygen uptake versus complex concentration for $Mn(PBu^n_3)I_2$ in THF. The slope of this plot is almost exactly 1, and the intercept represents the amount of dioxygen absorbed by the 100 cm^3 THF, which coincides with our separate blank studies on THF. Quantitative dioxygen absorption (67 cm^3 of O_2 over the THF blank) by some $Mn(PEt_3)X_2$ complexes in THF are

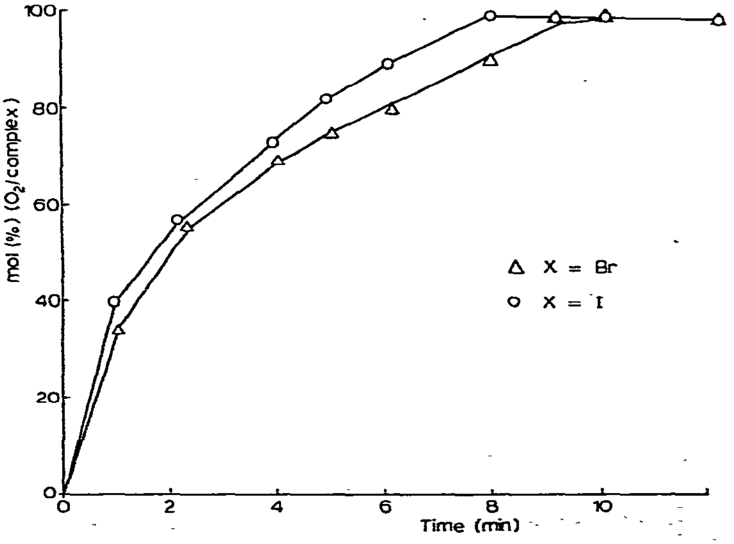


Fig. 2. Rate of dioxygen uptake by 3 × 10^{-3} mole $Mn(PEt_3)X_2$ in 100 ml THF at 0°C.

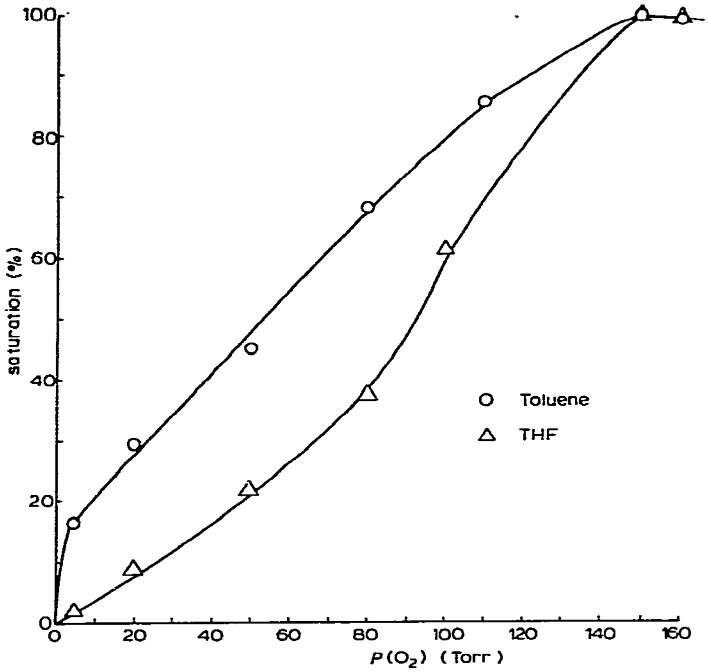


Fig. 3. Solution isotherms for $Mn(PPr^n_3)Cl_2$ at 20°C.

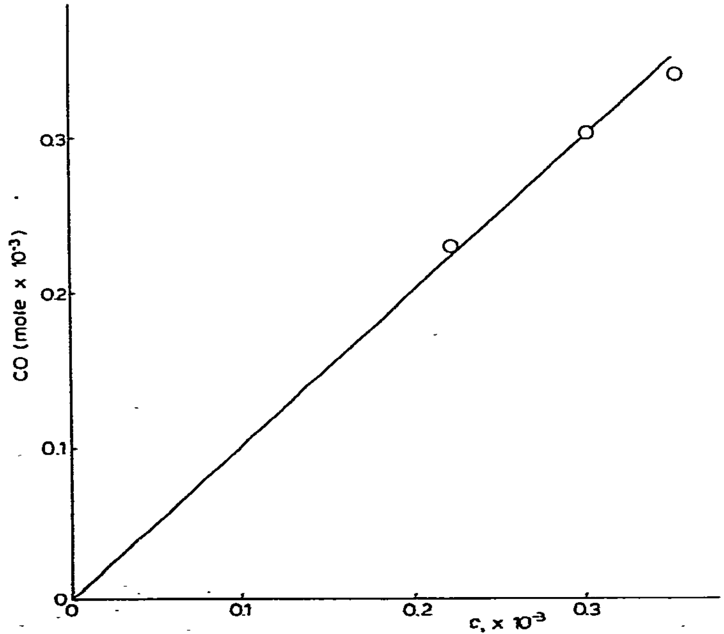


Fig. 4. CO uptake by $Mn(PPhMe_2)Cl_2$ at 0°C using different concentrations of the complex in THF (blank THF absorption subtracted).

shown in Fig. 2. These experiments clearly show the formation of a 1/1 complex, $Mn(PR_3)(O_2)X_2$, in THF solution. Careful studies have actually allowed us to construct isotherms (dioxygen-binding curves), some of which are shown in Fig. 3.

We are expanding our interests now to the reaction of other small molecules with $Mn(PR_3)X_2$. Figure 4 is a plot of carbon monoxide absorbed versus the concentration of $Mn(PPhMe_2)Cl_2$ in THF. The slope is 0.98, indicating the formation of $Mn(PPhMe_2(CO)Cl_2$. The reaction is reversible. Typically, the $\nu(CO)$ band in free CO moves to 2100—2085 cm^{-1} in the complexes [20].

Conclusion

Green, Mingos and their co-workers [1] claimed that their experiments produced highly coloured manganese(III) (or mixed valence state manganese) and phosphine oxides. The experiments they describe would undoubtedly give these products, and their observations are broadly in agreement with our own published work on manganese(III)-phosphine oxides [2,6] in papers not cited by them. Like Green et al., we have never observed dioxygen binding by phosphine oxide complexes of manganese in any oxidation state.

Green and Mingos and their colleagues [1] imply that their observations have relevance to our own work on $Mn(PR_3)X_2$ complexes and their ability to bind small molecules reversibly [3,6,14—21]. We strongly disagree with this implication. Under the unsuitable conditions they employ there is little chance of the formation or subsequent stable existence of $Mn(PR_3)X_2$, and, by their own admission, they could not have measured quantitative dioxygen absorption even if their reaction products had permitted it.

Acknowledgment

I am grateful to many colleagues for their comments on the paper by Green, Mingos and co-workers [1].

References

1 R.M. Brown, R.E. Bull, M.L.H. Green, P.D. Grebenik, J.J. Martin-Polo and D.M.P. Mingos, J. Organometal. Chem., 201 (1980) 437.
2 W. Levason and C.A. McAuliffe, J. Inorg. Nucl. Chem., 37 (1975) 340.
3 C.A. McAuliffe, H. Al-Khateeb, M.H. Jones, W. Levason, K. Minten, J. Chem. Soc. Chem. Commun, (1979) 736.
4 S. Casey, W. Levason and C.A. McAuliffe, J. Chem. Soc. Dalton, (1974) 886.
5 M.H. Jones, W. Levason, C.A. McAuliffe and M.J. Parrott, J. Chem. Soc. Dalton, (1976) 1642.
6 A. Hosseiny, C.A. McAuliffe, K. Minten, M.J. Parrott, R. Pritchard and J. Tames, Inorg. Chim. Acta, 39 (1980) 227.
7 G. Wilkie, H. Schott and P. Heimbach, Angew. Chem. Intern. Ed., 6 (1967) 92.
8 D.D. Schmidt and J.T. Yoke, Inorg. Chem., 9 (1970) 1176.
9 L. Vaska, Science, 140 (1963) 809.
10 C.A. McAuliffe and R.J. Pollock, J. Organometal. Chem., 77 (1974) 265.
11 V.J. Choy and C.J. O'Connor, Coord. Chem. Rev., 9 (1972) 145.
12 A. Hosseiny, A.G. Mackie, C.A. McAuliffe and K. Minten, Inorg. Chim. Acta, 49 (1981).
13 H. Funk and H. Kreis, Z. Anorg. Chem., 349 (1967) 45.
14 C.A. McAuliffe, H. Al-Khateeb, D.S. Barratt and A. Hosseiny, J. Chem. Soc. Dalton, submitted, Paper 1/1171.

15 C.A. McAuliffe, A. Hosseiny and K. Minten, J. Chem. Soc. Dalton, submitted, Paper 1/1173.
16 C.A. McAuliffe, M.G. Little and B.J. Raynor, J. Chem. Soc. Chem. Commun., in press.
17 M. Barber, R.S. Bordoli, A. Hosseiny, K. Minten, C.R. Perkin, R.D. Sedgwick and C.A. McAuliffe, Inorg. Chim. Acta, 45 (1980) L89.
18 C.A. McAuliffe and H. Al-Khateeb, Inorg. Chim. Acta, 45 (1980) L195.
19 C.A. McAuliffe, W. Levason and F.P. McCullough, Patent (PCT)GB 79/00038, September 25, 1978.
20 C.A. McAuliffe, A. Hosseiny and K. Minten, manuscript in preparation.
21 C.A. McAuliffe in Proceedings of the 2nd B.O.C. Priestley Conference, Birmingham University, September 1980, Special Publication of the Royal Society of Chemistry, p. 119, 1981.

Comments on the paper by Dr. C.A. McAuliffe

1. We did not attempt the syntheses of the compounds $Mn(PR_3)X_2$ in the presence of dioxygen but in high purity dinitrogen. A recrystallised and analytically pure sample of the compound $MnBr_2(THF)_2$ was used and not the commercial $MnBr_2$. We took considerable precautions to reduce the water content of our materials and solvents, as described in our paper.

2. The reference 6 to which we did not refer had a publication date shortly before our submission and thus we overlooked this paper. The paper states that $MnBr_2(THF)_2$ in tetrahydrofuran with one mole of PMe_2Ph gives an "active" haem analogue which when dioxygenated has an electronic spectrum *identical* to that of an *authentic* haem analogue. It seems *very probable indeed* that *our* $MnBr_2(THF)_2/PMe_2Ph$ system in tetrahydrofuran is identical to this system.

3. The analytically pure $MnBr_2(THF)_2$ was used for electrochemical studies and was not *certainly hydrated.* Our electrochemical oxidation on the $MnBr_2(THF)_2/PBu^n_3$ system was *also* carried out in *tetrahydrofuran* and gave spectra *identical,* except for the extinction coefficient, to that published (ref. 3). Dr. McAuliffe notes that we refer also to a maximum at 560 nm but does not note that this refers to a different system, i.e. using PMe_2Ph in *MeCN.*

4. The 20% error we cite on p. 441, lines 1—8 refers to the 4 cm^3 *increase* in uptake of dioxygen and *not* to the total volume, i.e. 176 + 4 cm^3. Thus we find only minor dioxygen uptake. If the dioxygen had reacted with the PBu^n_3 at a measurable rate then we would have observed this as stoichiometric uptake of dioxygen. The experiment shows that the reaction between dioxygen and PBu^n_3 in the presence of $MnBr_2(THF)_2$ in tetrahydrofuran solution at —63°C is very slow.

There is an error on p. 443, paragraph 2 of our paper and it was *tetrahydrofuran* and not toluene which was removed.

Concerning the Method (a) for determination of the extinction coefficient. If the compound $Mn(PBn^n_3)Br_2$ was present in equilibrium in solutions of PBu^n_3 and $MnBr_2(THF)_2$ in tetrahydrofuran then an excess of PBu^n_3 should increase the equilibrium concentration. A *measured* quantity of dioxygen was added and was completely dissolved. Dr. McAuliffe quite correctly draws attention to the erroneous equation $O_2 + 2\ Mn^{2+} \rightleftharpoons MnO_2{}^{2+}$ which clearly should read as $O_2 + Mn^{2+} \rightleftharpoons Mn^{2+}O_2$. The minimum value of the extinction coefficient (at 570 nm) was found to be 34 times greater than that reported (ref. 3.)

In experiment (a), p. 444, in fact we said, "Our apparatus was not calibrated in a manner which would enable us to eliminate small errors arising from