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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 changes in atmospheric pressure although these were monitored". The atmospheric pressure changes were very small and the errors arising were included in the error estimates given. In experiment (b), p. 444, the rate of oxidation of PBu^n_3 in tetrahydrofuran at —63°C is very slow. The development of the blue-purple colour was not accompanied by significant uptake of dioxygen.

5. It is clear that our paper is written too briefly; it contains a typographical error (2 MnO^{2+}), an error (toluene for tetrahydrofuran) and some ambiguities and is open to misinterpretation. We hope that we have been able to clarify these matters. We have considered *all* the points raised by Dr. McAuliffe but we do not, as a result, wish to alter our main conclusions which are based on the experiments described in our paper. A full discussion of the above paper will appear in the D. Phil. thesis of Mr. J.J. Martin-Polo.

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

M.L.H. GREEN