Letters

Comments on the attempts by Wickens and Abrams to synthesize manganese(II) phosphine complexes

The recent paper by Wickens and Abrams[1] entitled 'On The Synthesis of Dimethylphenylphosphine Complexes of Manganese(II) Halides' contributes nothing but confusion on the topic it purports to clear up.

Evidently the authors have not read our work on the syntheses and characterization of the $[MnLX_2]$ complexes prepared by treating MnX_2 surfaces with phosphine vapour.[2,3] These complexes were evacuated to 10^{-6} Torr ($\approx 1.3 \times 10^{-4}$ Pa) routinely with no loss of phosphine. Therefore I must assume that the solids prepared by these workers contained free phosphine, since they made the comment that their solids lost phosphine upon evacuation making it impossible accurately to determine O_2 uptake. Furthermore, we have shown that under pure oxygen at ambient temperature decomposition of the compounds to phosphine oxide complexes does occur. Hence it is not surprising that the solid-state mixtures reported by these workers did not bind O_2 reversibly.

While all of our reported work has been in the solid state we have studied solutions of the complexes; some of these results are in the form of a patent.[4] Of interest is our observation that the compounds can be synthesized as described by McAuliffe[5,6] provided appropriate care is taken to exclude moisture. We should point out that solutions of $[Mn(PMe_2Ph)X_2]$ in tetrahydrofuran are dark green and not red as indicated by Wickens and Abrams.[1] Furthermore, we found that reversible uptake of O_2 was possible in solution at -80 °C. At this temperature a large number of reversible cycles could be carried out. At higher temperatures (*e.g.*, 0 °C) in a dioxygen atmosphere, some decomposition of the complex was observed.

It is unfortunate that further confusion in this area will result from this work.[1]

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Wickens and Abrams reply. The vituperative tone adopted by Dr. Hill disguises the fundamental agreement between our results, and he is apparently confused as to the modest purpose of the work reported. Its sole objective was to amplify the experimental conditions necessary to duplicate the original syntheses of McAuliffe and co-workers[6,7] in the light of potential commercial uses.[8] As the work of McAuliffe was mostly in the form of Notes, Letters, or preliminary communications, details were necessarily somewhat brief. Our publication was an attempt to rationalize the failure of the dissenters[9] to replicate the wet chemistry synthesis.

On the first experimental point raised by Dr. Hill, that of stability, we still see no irreconcilable difference. Pumping to a pressure of *ca.* 1.5×10^{-3} (ref. 2) or 1.5×10^{-4} Pa (ref. 3) reflects only a dynamic balance between pumping speed and rate of evolution of vapour. In practice we have observed 'hard *vacua*' at room temperature in kinetically slow desorption of physically sorbed gases from carbon where several per cent by weight was eventually liberated. Weight monitoring to the necessary accuracy would not be reasonably possible for equipment such as that used by Dr. Hill (*e.g.*, ref. 2, note 5) and extra free manganese halide would not be detectable.

Only on Dr. Hill's second experimental point can I fail to agree with him. We consistently observed the colour change to wine red on admission of oxygen to manganese iodide–tertiary phosphine–tetrahydrofuran systems. A change to bottle green was indeed observed with all other solvents; its visible spectrum was part of a consistent series with the manganese bromide (royal blue) and chloride (lilac) complexes. The solid-state diffuse reflectance spectra of the colours obtained on exposure of the equivalent solids to dry air (<1 p.p.m. H_2O) were essentially identical to the solvent system transmission spectra except in the case of tetrahydrofuran. The green colour was not sensitive to the presence of moisture and could even be obtained in the system air–diethyl ether–tri-n-butylphosphine–manganese(II) iodide tetrahydrate.

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