# Cyclic Voltammetric Studies on Some Manganese(II) Tertiary Arylphosphine Complexes

**Guang Quing Li, Charles A. McAuliffe,* Anthony G. Mackie, Philomena P. Mac Rory and Peter T. Ndifon**
*Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, UK*

A series of manganese(II) arylphosphine complexes, $[\{Mn[P(aryl)_3]X_2\}_n]$ [aryl = Ph, 4-$ClC_6H_4$, 4-$MeC_6H_4$, 4-$MeOC_6H_4$ or 2,4,6-$(MeO)_3C_6H_2$; X = Cl, Br, I or NCS], have been synthesised and characterised. At ambient temperature all the complexes are inactive towards dioxygen binding, but at 228 K a toluene solution of $[Mn\{P(C_6H_4OMe\text{-}4)_3\}I_2]$ absorbs 1 mol of $O_2$ per mol of complex; this represents the first triarylphosphine manganese(II) complex to bind dioxygen. Cyclic voltammetric studies on these compounds suggest a one-electron transfer process which becomes more reversible as the temperature is lowered, thus indicating an electrochemical–chemical mechanism, with $E^{\circ\prime}$ values influenced by both the anion and phosphine ligands.

Our interest in manganese(II) tertiary phosphine complexes stems from the observation that they are able reversibly to bind dioxygen and other small molecules either in the solid state or in solution.[1–3] The ability of these compounds to bind dioxygen in solution is generally in the order $PR_3$ (R = alkyl group) > $PPhR_2$ > $PPh_2R$ ≫ $PPh_3$ (no activity). Manganese(II) triphenylphosphine complexes do not bind oxygen even under high dioxygen partial pressure.[4] It has also been shown that while complexes of the form $[Mn(PR_3)(NCS)_2]$ readily and reversibly react with dioxygen, those of the phenyl-substituted phosphines $[Mn(PPh_{3-n}R_n)(NCS)_2]$ ($n$ = 1 or 2) are inactive towards dioxygen binding.[1,5]

When the $Mn(phosphine)X_2$ complexes co-ordinate dioxygen they colour vividly; removal of the dioxygen causes the compounds to revert to their original pale colour [equation (1)].

$$\underset{\text{(pale)}}{\mathrm{Mn(phosphine)X_2}} \underset{-O_2}{\overset{+O_2}{\rightleftharpoons}} \underset{\text{(deeply coloured)}}{\mathrm{Mn(phosphine)X_2(O_2)}} \tag{1}$$

This is presumably due to the removal of an electron(s) from the manganese(II). It might thus be expected that the ease of electrochemical oxidation/reduction of these complexes may be related to the ability of $O_2$ to remove/return an electron(s) from the metal.

We report here a series of manganese(II) tertiary arylphosphine complexes, $[Mn(PR_3)X_2]$ [X = Cl, Br, I or NCS; R = Ph, 4-$ClC_6H_4$, 4-$MeC_6H_4$, 4-$MeOC_6H_4$ or 2,4,6-$(MeO)_3C_6H_2$], Table 1, and some cyclic voltammetry studies thereupon. The 4-substituted ligands used were chosen for their similar steric properties, *i.e.* similar cone angles, but differing electronic properties resulting in different basicities.

## Experimental

The manganese(II) complexes were prepared, and the dioxygen uptake measured, as reported previously.[1] Elemental analyses and some physical data are given in Table 1.

Cyclic voltammetry measurements[6,7] were carried out using a model 362 EG and G PAR potentiostat in conjunction with a three-electrode cell fitted with a purge-gas inlet and outlet and consisting of a platinum wire working electrode, a Ag–AgCl reference electrode and a platinum auxiliary electrode. The cyclic voltammograms were recorded from *ca.* $10^{-3}$ mol dm$^{-3}$ solutions of $[\{Mn(PR_3)X_2\}_n]$ complexes in dry degassed methylene chloride (BDH AR grade, purified according to published method[8]), and containing approximately 0.2 mol dm$^{-3}$ supporting electrolyte ($NBu^n_4PF_6$). The voltammograms were recorded on a Linseis LY 1800 X-Y recorder. All the electrochemical experiments were performed under argon at temperatures ⩽293 K. The solutions were cooled in a toluene–solid $CO_2$ mixture. The data ($E^a_p$, $E^c_p$, $E^{\circ\prime}$, $i_p^c/i_p^a$ and $iR_u$ compensation) were processed using the convolution–deconvolution transform technique aided by the available package of computer programs.[9]

## Results and Discussion

The ability of manganese(II) salts to form complexes with tertiary arylphosphines appears to be strongly influenced by the electronic properties of the ligands. While tris(4-methoxyphenyl)phosphine readily forms complexes, tris(4-chlorophenyl)phosphine does not appear to react under the same conditions. The time necessary for complete complex formation with $PR_3$ is in the order: R = 2,4,6-$(MeO)_3C_6H_2$ (p$K_a$ = 11.2) < 4-$MeOC_6H_4$ (p$K_a$ = 4.57) < 4-$MeC_6H_4$ (p$K_a$ = 3.84) < Ph (p$K_a$ = 2.73) ≪ 4-$ClC_6H_4$ (p$K_a$ = 1.03), which also reflects the order of decreasing basicity of the phosphine ligands.[10,11]

*Dioxygen Binding.*—We have previously reported that the complexes $[\{Mn(PPh_3)X_2\}_n]$ (X = Cl, Br, I, or NCS) do not bind dioxygen in the solid state or in solution.[4] Here we report similar studies using more basic ligands. Since the substituents in $P(C_6H_4Me\text{-}4)_3$ and $P(C_6H_4OMe\text{-}4)_3$ are in the *para* position, these ligands have the same cone angles ($\theta$ = 145) as does triphenylphosphine.[10] In contrast very bulky $P[C_6H_2(OMe)_3\text{-}2,4,6]_3$ ($\theta$ = 212°) is one of the most basic phosphine ligands (p$K_a$ = 11.2). At room temperature the complexes $[\{Mn(PR_3)X_2\}_n]$ [R = Ph, 4-$MeC_6H_4$, 4-$MeOC_6H_4$ or 2,4,6-$(MeO)_3C_6H_2$; X = Cl, Br, I or NCS] do not bind dioxygen. However, at 228 K, one of the complexes, $[Mn\{P(C_6H_4OMe\text{-}4)_3\}I_2]$, was found to bind dioxygen reversibly, forming greenish blue solutions. The oxygenated reaction was reversed by gently warming the solution or by applying a vacuum.

This complex binds dioxygen in a 1:1 ratio over a range of concentrations. Fig. 1 contains a plot of $O_2$ absorbed *vs.* concentration of complex; the slope is 0.98 and the intercept at

**Table 1** Physical properties and elemental analyses for some arylphosphine manganese(II) dihalide complexes

| | | | | Analysis (%)* | | | |
|---|---|---|---|---|---|---|---|
| Complex | Colour | M.p./°C | $\mu_{eff}^{rt}$ | C | H | X | P |
| $[Mn\{P(C_6H_4OMe-4)_3\}Cl_2]$ | White | 124–125 | 5.89 | 52.5 (52.7) | 4.7 (4.4) | 12.6 (14.8) | 6.3 (6.5) |
| $[Mn\{P(C_6H_4OMe-4)_3\}Br_2]$ | Off-white | 120–122 | 5.85 | 44.4 (44.5) | 3.9 (3.7) | 26.8 (28.2) | 5.2 (5.5) |
| $[Mn\{P(C_6H_4OMe-4)_3\}I_2]\cdot C_5H_{12}$ | Pink-orange | 148–151 (decomp.) | 5.72 | 42.1 (42.5) | 3.7 (4.2) | 34.6 (34.6) | 3.8 (4.2) |
| $[Mn\{P(C_6H_4OMe-4)_3\}(NCS)_2]$ | Pale yellow | 125–126 | 5.72 | 52.5 (52.7) | 4.2 (4.0) | 5.1 (5.4) | 5.9 (5.9) |
| $[Mn\{P[C_6H_2(OMe)_3-2.4.6]_3\}Cl_2]$ | White | 138–140 (decomp.) | 5.88 | 48.7 (49.2) | 5.4 (5.0) | 10.0 (10.8) | 4.2 (4.7) |
| $[Mn\{P[C_6H_2(OMe)_3-2.4.6]_3\}Br_2]$ | Pale pink | 135–136 | 5.81 | 42.7 (43.4) | 5.4 (4.4) | 22.0 (21.4) | 4.0 (4.2) |
| $[Mn\{P[C_6H_2(OMe)_3-2.4.6]_3\}I_2]$ | Brown | 125–127 (decomp.) | 5.50 | 38.6 (38.5) | 4.2 (3.9) | 30.2 (30.2) | 3.8 (3.7) |
| $[Mn\{P[C_6H_2(OMe)_3-2.4.6]_3\}(NCS)_2]$ | Pale yellow | 62–64 (decomp.) | 5.55 | 49.7 (49.5) | 4.6 (4.7) | 3.9 (4.0) | 4.3 (4.4) |
| $[Mn\{P(C_6H_4Me-4)_3\}Cl_2]$ | White | 260 (decomp.) | 5.87 | 60.0 (58.6) | 4.7 (4.9) | 15.9 (16.5) | 7.0 (7.2) |
| $[Mn\{P(C_6H_4Me-4)_3\}Br_2]$ | Off-white | 251 (decomp.) | 5.68 | 47.4 (48.6) | 3.9 (4.0) | 30.5 (30.8) | 6.0 (6.0) |
| $[Mn\{P(C_6H_4Me-4)_3\}I_2]$ | Pink | 188–190 | 5.91 | 40.8 (41.1) | 4.1 (3.4) | 41.0 (41.4) | 4.8 (5.0) |
| $[Mn\{P(C_6H_4Me-4)_3\}(NCS)_2]$ | Pale yellow | 230 (decomp.) | 5.36 | 57.8 (58.1) | 4.3 (4.4) | 5.6 (5.9) | 6.2 (6.5) |
| $[Mn\{PPh(C_6H_4OMe-2)_2\}I_2]$ | Pink | 180–181 | 5.49 | 38.3 (38.0) | 3.1 (3.0) | 38.4 (40.2) | 4.7 (4.9) |
| $[Mn\{PPh(C_6H_4OMe-2)_2\}(NCS)_2]$ | Pale yellow | 180–182 | 5.34 | 51.6 (52.5) | 3.7 (3.9) | 5.7 (5.7) | 6.0 (6.3) |
| $[Mn(PPh_3)I_2]$ | Pink | 195–196 | 5.83 | 38.0 (37.8) | 2.9 (2.6) | 44.2 (44.5) | 5.2 (5.4) |

* Calculated values in parentheses; X = Cl, Br, I or N.

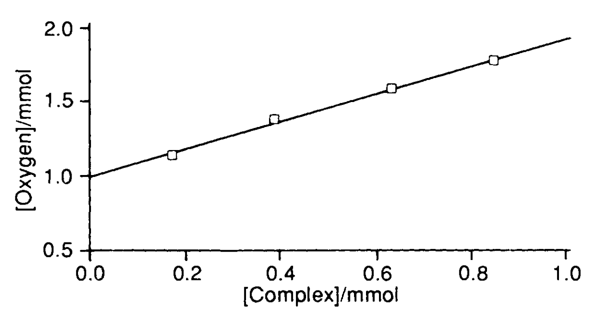

**Fig. 1** Plot of $O_2$ absorbed *versus* $[Mn\{P(C_6H_4OMe-4)_3\}I_2]$ concentration in toluene at 228 K

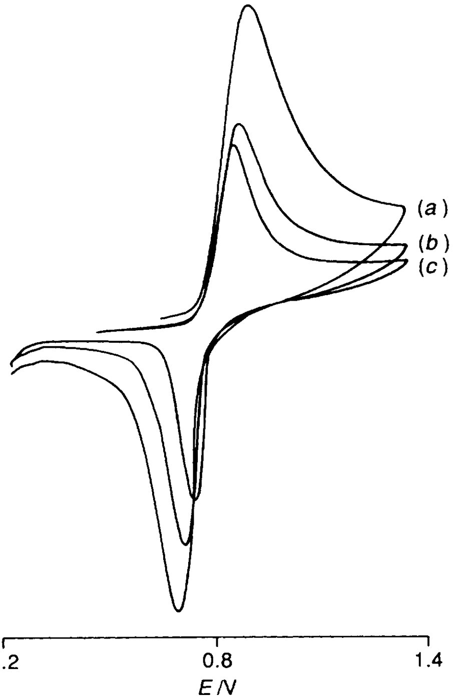

**Fig. 2** Cyclic voltammograms for *ca.* $10^{-3}$ mol dm$^{-3}$ $[Mn\{P(C_6H_4OMe-4)_3\}I_2]$ in $CH_2Cl_2$–0.2 mol dm$^{-3}$ $NBu_4PF_6$ *vs.* Ag–AgCl at (*a*) 0.2, (*b*) 0.1 and (*c*) 0.05 V s$^{-1}$

zero concentration, $9.4 \times 10^{-4}$ mol $O_2$, is in excellent agreement with the independently measured blank ($9.5 \times 10^{-4}$ mol $O_2$). This is the first example of a (triarylphosphine)-manganese(II) complex to exhibit reversible dioxygen binding. In view of the electrochemical work, the dioxygen absorptions were repeated using methylene chloride solvent with and without added $NBu_4PF_6$. No significant effects were noted.

The inactivity of $PPh_3$ complexes ($\theta = 145°$) must now be ascribed to electronic, rather than steric, factors although the latter can be invoked to rationalise the inactivity of the complexes derived from the strongly basic tris(2,4,6-trimethoxyphenyl)phosphine ($\theta = 212°$), *i.e.* the critical (or minimum) deactivating cone angle $\theta$ is $> 145$ and $\leqslant 212°$. The lower limit of the p$K_a$ of the phosphine moiety has also been redefined as *ca.* 4.57. The balance between steric and electronic factors of the phosphine moieties for the dioxygen binding ability of the complexes is becoming more clearly defined.

*Cyclic Voltammetry Studies.*—Inasmuch as the interactions of Mn(phosphine)$X_2$ complexes with dioxygen is thought to involve the removal of an electron(s) from the manganese(II) centre resulting in the formation of the observed highly coloured species, the electrochemical oxidation/reduction of these compounds, although mechanistically distinct, may be collated to their ability to bind dioxygen reversibly.

The cyclic voltammograms for most of the iodo complexes (see Figs. 2 and 3) suggest a reversible one-electron transfer process, with peak-current ratios, separations and dependence on scan rates typical of diffusion-controlled processes [equation (2)]. The cyclic voltammograms of the bromo-, chloro- and thiocyanato complexes indicate that the electrochemical behaviour is overlaid by one or more chemical processes resulting in 'loss' of electrochemical reversibility, Table 2. In the case of the iodo complexes these effects were separated.

$$[Mn^{II}\{P(aryl)_3\}X_2] \rightleftharpoons [Mn^{III}\{P(aryl)_3\}X_2]^+ + e \quad (2)$$

Fig. 3 shows the cyclic voltammogram for $[Mn\{P[C_6H_2(OMe)_3-2,4,6]_3\}I_2]$ at 293, 273 and 253 K. The observed absence of a reduction peak corresponding to the oxidation peak at room temperature suggests that the electrochemically oxidised species, $[Mn^{III}\{P(aryl)_3\}X_2]^+$, undergo some chemical reaction to yield unidentified products, which are electrochemically inactive. However, as the temperature is lowered, the reduction peak grows significantly and shows an electrochemically reversible behaviour at 253 K, suggesting that the oxidised species become stable to chemical reaction at low temperature, and thus is capable of being electrochemically reduced to give the observed reversible behaviour. This behaviour suggests an electrochemical–chemical (e.c.) mechanism[6,7] in which a

**Table 2** Cyclic voltammetry data for solutions of manganese(II) tertiary arylphosphine complexes in $CH_2Cl_2$ (scan rate 100 mV $s^{-1}$)[a,b]

| Complex | $E_p^a$/V | $E_p^c$/V | $\Delta E$/V | $E^{\circ\prime}$/V | $i_p^c/i_p^a$ |
|---|---|---|---|---|---|
| $[Mn\{P(C_6H_4OMe\text{-}4)_3\}(NCS)_2]$ | 0.686 | 0.623 | 0.063 | 0.655 | 0.917 |
| $[Mn\{P[C_6H_2(OMe)_3\text{-}2,4,6]_3\}(NCS)_2]$ | 0.719 | 0.654 | 0.065 | 0.687 | 0.935 |
| $[Mn(PPh_3)I_2]$ | 0.56 | 0.491 | 0.069 | 0.526 | 0.730 |
| $[Mn\{PPh(C_6H_4OMe\text{-}2)_2\}I_2]$ | 0.739 | 0.675 | 0.064 | 0.707 | 0.962 |
| $[Mn\{P(C_6H_4Me\text{-}4)_3\}I_2]$ | 0.772 | 0.711 | 0.061 | 0.741 | 0.990 |
| $[Mn\{P(C_6H_4OMe\text{-}4)_3\}I_2]$ | 0.801 | 0.736 | 0.065 | 0.769 | 0.870 |
| $[Mn\{P[C_6H_2(OMe)_3\text{-}2,4,6]_3\}I_2]$[c] | 0.859 | 0.794 | 0.065 | 0.827 | 0.901 |
| $[Mn\{P[C_6H_2(OMe)_3\text{-}2,4,6]_3\}Br_2]$ | 1.15 | 1.08 | 0.07 | 1.11 | 0.570 |
| $[Mn\{PC_6H_4OMe\text{-}4)_3\}Br_2]$ | 1.38 | 1.32 | 0.06 | 1.34 | 0.699 |
| $[Mn\{PC_6H_4OMe\text{-}4)_3\}Cl_2]$ | 1.45 | 1.37 | 0.08 | 1.41 | 0.550 |
| $[Mn\{P[C_6H_2(OMe)_3\text{-}2,4,6]_3\}Cl_2]$ | 1.70 | 1.64 | 0.06 | 1.67 | 0.606 |

[a] Under these conditions ferrocene showed a reversible voltammogram at $E^{\circ\prime}$ = 0.45 V *vs.* Ag–AgCl with a peak-to-peak separation $\Delta E$ = 0.060 V. [b] Potentials *vs.* Ag–AgCl reference electrode. [c] Measurements at 253 K.

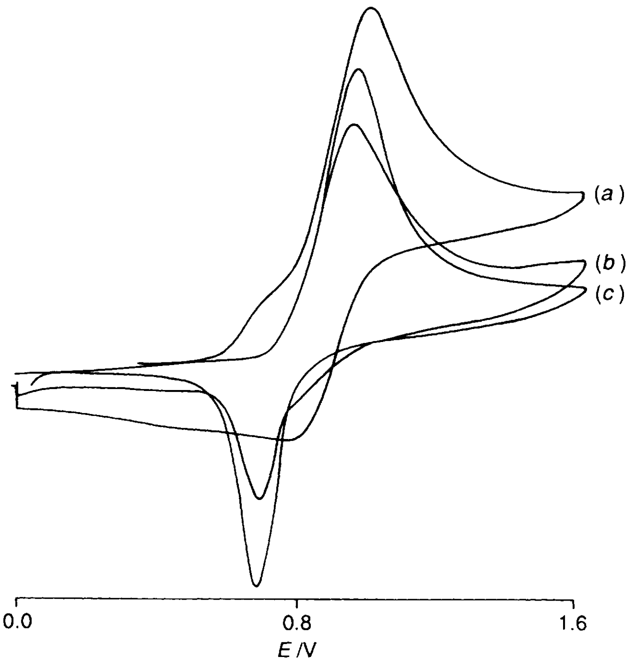

**Fig. 3** Cyclic voltammograms for *ca.* $10^{-3}$ mol $dm^{-3}$ $[Mn\{P[C_6H_2(OMe)_3\text{-}2,4,6]_3\}I_2]$ in $CH_2Cl_2$–0.2 mol $dm^{-3}$ $NBu_4PF_6$ *vs.* Ag–AgCl at (*a*) 293, (*b*) 273 and (*c*) 253 K

chemical reaction accompanies the electrochemical process and the rate of this chemical reaction is greatly reduced as the temperature is lowered.

No meaningful coulometric measurements could be made on these complexes because of very low solubility in methylene chloride. The formal electrode potentials, $E^{\circ\prime}$, for these $Mn^{3+}$–$Mn^{2+}$ couples range between 0.65 and 1.67 V and depend on the nature of the ligands co-ordinated to manganese. The values decrease as expected in the order Cl > Br > I > NCS which is the order of decreasing electronegativity of the halides (Cl > Br > I). Such behaviour has also been observed for manganese(II) porphyrin complexes.[12] While these $E^{\circ\prime}$ values do not reflect the expected σ-donor properties of the phosphine ligands they increase with the bulkiness of these ligands.

The compound $[Mn\{P(C_6H_4OMe\text{-}4)_3\}I_2]$ shows a reversible electrochemical behaviour ($E^{\circ\prime}$ = 0.769 V and $i_p^c/i_p^a$ = 0.870), Fig. 2. One would expect all the complexes showing similar electrochemical behaviour ($E^{\circ\prime}$ = 0.7–0.8 V) to exhibit similar reactivity towards dioxygen as does this compound but this is not the case and no electrochemical explanation is evident.

We have, however, previously observed that both the electronic and steric properties of tertiary phosphine ligands act together to influence the behaviour of $Mn(PR_3)X_2$ complexes,[5] in particular, their ability to bind dioxygen.[1,4] The $E^{\circ\prime}$ values for these compounds therefore depend on the synergic electronic and steric effects of the phosphine ligands.

## References

1 C. A. McAuliffe, H. F. Al-Khateeb, D. S. Barratt, J. C. Briggs, A. Challita, A. Hosseiny, M. G. Little, A. G. Mackie and K. Minten, *J. Chem. Soc., Dalton Trans.*, 1983, 2147.
2 C. A. McAuliffe, *J. Mol. Catal.*, 1988, **44**, 35.
3 D. S. Barratt, G. A. Gott and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 1988, 2065.
4 A. Hosseiny, A. G. Mackie, C. A. McAuliffe and K. Minten, *Inorg. Chim. Acta*, 1981, **49**, 99.
5 K. Minten and C. A. McAuliffe, unpublished work.
6 R. Greef, R. Peat, L. M. Peter, D. Pletcher and J. Robinson, in *Instrumental Methods in Electrochemistry*, Ellis Horwood, Chichester, 1985.
7 A. J. Bard and L. R. Faulker, in *Electrochemical Methods, Fundamentals and Applications*, Wiley, New York, 1980.
8 K. M. Kadish and J. M. Anderson, *Pure Appl. Chem.*, 1987, **59**, 703; S. E. Creager and R. W. Murray, *Inorg. Chem.*, 1987, **26**, 2612.
9 Condecon(TM) 300 cyclic voltammetry software for EG and G 362 potentiostat, EG and G Instruments, Wokingham, Berks., 1986.
10 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313; C. A. McAuliffe, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1987, vol. 2, pp. 989–1060.
11 M. Wada, S. Higashizaki and A. Tsubio, *J. Chem. Res.*, 1985, 38.
12 L. J. Boucher and J. K. Garba, *Inorg. Chem.*, 1970, **9**, 2644.

*Received* 24*th October* 1991; *Paper* 1/05430I