The Reversible One-electron Oxidation of *trans*-[Mn^{I}L(CO)(Ph$_2$PCH$_2$PPh$_2$)$_2$]$^{z+}$: Synthesis and Characterisation of Stable Manganese(II) Derivatives *

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The complexes *trans*-[MnL(CO)(dppm)$_2$]^z (**1**; z = 0, L = Br, CN, or NCS; z = +1, L = NCMe, CNMe, CNBu^t, or CO; dppm = Ph$_2$PCH$_2$PPh$_2$) undergo diffusion-controlled, one-electron oxidation at a platinum electrode in CH$_2$Cl$_2$. The observed linear correlation between oxidation potential, E^0, and ligand constant, P_L, has allowed (*i*) a comparison of the electron-richness and polarisability of the binding site [Mn(CO)(dppm)$_2$]$^+$ with those of related square-pyramidal species, and (*ii*) comments to be made concerning the linkage isomerism of the thiocyanate ligand. All of the manganese(II) complexes *trans*-[MnL(CO)(dppm)$_2$]$^{z+1}$ (**2**) except for the bromide (**2**; z = 0, L = Br) have been generated by chemical oxidation (with [NO][PF$_6$] or [N$_2$C$_6$H$_4$F-*p*][PF$_6$]) or by controlled potential electrolysis. The paramagnetic compounds have been characterised by i.r. and e.s.r. spectroscopy, and (**2**; z = +1, L = CNMe or CNBu^t) have been isolated as crystalline salts of the [PF$_6$]$^-$ anion. The irreversible oxidation of (**1**; z = 0, L = Br), either electrolytically or by [Fe(η-C$_5$H$_5$)$_2$][PF$_6$] in CH$_2$Cl$_2$, leads to the formation of (**1**; z = +1, L = CO), but in the presence of acetonitrile or CNBu^t the reaction gives (**1**; z = +1, L = NCMe or CNBu^t).

Electrochemical studies on manganese and rhenium carbonyl derivatives[1] have led *inter alia* to the discovery of two important reactions, namely oxidatively-induced isomerisation[2] and photo-induced electron transfer.[3] The former has provided a route to otherwise inaccessible geometric isomers,[4] for example, *trans*-[MnBr(CO)$_2$L(L–L)] [L = phosphine or phosphite, L–L = dppm (Ph$_2$PCH$_2$PPh$_2$) or dppe (Ph$_2$PCH$_2$CH$_2$PPh$_2$)] from the *cis,cis*-analogue;[5] the latter is involved in the reduction of CO$_2$ to CO mediated by *fac*-[ReX(CO)$_3$(bipy)] (X = Cl or Br, bipy = 2,2′-bipyridyl).[6]

Our long-standing interest[7–9] in the chemistry of manganese carbonyl derivatives has occasionally led to the observation of redox reactions, and we have therefore begun a systematic electrochemical study of species such as *trans*-[MnL(CO)(dppm)$_2$], *cis,cis*- and *trans*-[MnL(CO)$_2${P(OPh)$_3$}(dppm)], and *cis,trans*-[MnL(CO)$_2${P(OPh)$_3$}(bipy)].

In this paper, we describe the chemical and electrochemical oxidation of the first of these series, namely *trans*-[MnL(CO)(dppm)$_2$]^z (**1**; z = 0, L = Br, CN, or NCS; z = +1, L = CO, NCMe, CNMe, or CNBu^t). The relative electron-richness of (**1**) has made possible the generation of the stable, paramagnetic manganese(II) derivatives *trans*-[MnL(CO)(dppm)$_2$]$^{z+1}$ (**2**), and their isolation in the cases of L = CNMe or CNBu^t (z = +1). In addition, the linear correlation observed between the oxidation potential, E^0, and the ligand constant, P_L,[10] of (**1**) has allowed the electron-richness and polarisability of the binding site [Mn(CO)(dppm)$_2$]$^+$ to be assessed, and comments to be made concerning the linkage isomerism of the thiocyanate ligand.

The results obtained with the simple complexes (**1**) have provided a basis for understanding the electron-transfer properties of more complex mono- and bi-nuclear derivatives,[11] including the redox-catalysed isomerisation of *trans*-[MnBr(CO)$_2${P(OPh)$_3$}(dppm)] to *cis,cis*-[MnBr(CO)$_2${P(OPh)$_3$}(dppm)].[12]

Results and Discussion

In CH$_2$Cl$_2$, the cyclic voltammetry of *trans*-[MnL(CO)(dppm)$_2$]^z (**1**; z = 0, L = CN or NCS; z = +1, L = NCMe, CNMe, CNBu^t, or CO) is straightforward. Each complex shows one fully reversible (i_{red}/i_{ox} = 1, for scan rates 50 < v < 500 mV s^{-1}), diffusion-controlled ($i_{ox}/v^{\frac{1}{2}}$ = constant for 50 < v < 500 mV s^{-1}) oxidation wave in the region 0.0 to 0.9 V (Table 1).† The analogous bromide complex (**1**; z = 0, L = Br) behaves somewhat differently, however, in that electrode coating appeared to cause some diminution of the oxidation wave height and reversibility was only observed when $v \geqslant$ 1 V s^{-1} (the E^0 value given in Table 1 was taken from the cyclic voltammogram with v = 1 V s^{-1}). The chemical and electrochemical oxidation of (**1**; z = 0, L = Br) is therefore discussed in a separate section below.

Controlled potential electrolysis and coulometry readily verified that in all cases (except the bromide) oxidation of (**1**) involves the loss of one electron and the formation of the manganese(II) derivatives *trans*-[MnL(CO)(dppm)$_2$]$^{z+1}$ (**2**). For example, the oxidation of (**1**; z = +1, L = NCMe) at a platinum gauze basket ($E_{applied}$ = 0.7 V) resulted in the passage of 0.96 F mol^{-1} and the formation of a purple solution with one *reduction* wave (cyclic and rotating platinum electrode voltammetry) at a potential identical to that for the oxidation of (**1**; z = +1, L = NCMe).

Although (**2**; z = +1, L = NCMe) has been further characterised spectroscopically it is not as stable in solution as other manganese(II) derivatives in the series, even under nitrogen. Voltammetry showed that it decomposes, apparently *via* a first-order process,[13] to a mixture of unidentified products not including (**1**; z = +1, L = NCMe).

The E^0 value for the oxidation of (**1**) to (**2**) (Table 1) depends qualitatively on the donor–acceptor properties of L and on the charge, z; the cations (E^0 = 0.4—0.9 V) are considerably more difficult to oxidise than the neutral molecules (E^0 = 0.0—0.1 V). However, these data may be used more quantitatively to assess the polarisability and electron-richness of the square-pyramidal binding site [Mn(CO)(dppm)$_2$]$^+$.

Pickett and co-workers[10] have shown for several series of octahedral metal complexes that the measured oxidation potential, $E_{\frac{1}{2}}^{ox}$, correlates linearly with a ligand constant, P_L,

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* *Non-S.I. unit employed:* G = 10^{-4} T.

† Some of the complexes showed second oxidation waves at potentials >1.0 V and/or reduction waves at potentials < −1.5 V. These irreversible processes were not further characterised.

Table 1. Cyclic voltammetric data for the one-electron oxidation of *trans*-$[MnL(CO)(dppm)_2]^z$

L	z	E^0/V^a	P_L/V^b
Br	0	0.00^c	−1.17
CN	0	0.07	−1.00
NCS	0	0.09	−1.03^d
NCMe	+1	0.45	−0.58
CNMe	+1	0.53	−0.43
CNBu^t	+1	0.54	
CO	+1	0.86	0.00

[a] Unless otherwise stated, the oxidation is a one-electron process and is diffusion-controlled, obeying the criterion $i/v^{\frac{1}{2}}$ = constant for scan rates, v, in the range 50—500 mV s^{-1}. All potentials are *versus* the aqueous s.c.e., at a platinum bead in CH_2Cl_2 with 0.1 mol dm^{-3} $[NBu^n{}_4][PF_6]$ as supporting electrolyte. Under these condition, the E^0 values for the couples $[Fe(\eta-C_5H_5)_2]^+$–$[Fe(\eta-C_5H_5)_2]$ and $[Fe(\eta-C_5Me_5)_2]^+$–$[Fe(\eta-C_5Me_5)_2]$ are 0.47 and −0.07 V respectively. [b] Ligand constants from ref. 10 unless stated otherwise. [c] Only reversible at scan rates ≥1 V s^{-1}. [d] Measured in this work, see text.

defined by equation (1). The correlation is described by equation (2), where E_s and β are taken respectively as measures

$$P_L = E_{\frac{1}{2}}^{ox}\{[Cr(CO)_5L]\} - E_{\frac{1}{2}}^{ox}\{[Cr(CO)_6]\} \qquad (1)$$

$$E_{\frac{1}{2}}^{ox} = E_s + \beta.P_L \qquad (2)$$

of the electron-richness and polarisability of the square-pyramidal binding site to which the ligand L is bound.

A plot of E^0 [$E_{\frac{1}{2}}^{ox}$ of equation (2)] for (**1**) (Table 1) *vs.* P_L (taken from ref. 10) is indeed linear, with R = 0.989.[*] However, the data for (**1**; z = 0, L = NCS) deviate considerably from the straight line and, if omitted, the correlation coefficient is improved, R = 0.997. Because we have found[11] similar discrepancies for the thiocyanate complexes in two other series, namely *cis,cis*- and *trans*-$[MnX(CO)_2\{P(OPh)_3\}(dppm)]^z$, we have reinvestigated the ligand constant P_L(NCS).

A preliminary cyclic voltammetric study of $[NBu^n{}_4]$-$[Cr(NCS)(CO)_5]$ showed an oxidation wave with $E_{\frac{1}{2}}^{ox}$ = 0.56 V. Taken with a potential of 1.53 V for the oxidation of $[Cr(CO)_6]$ to $[Cr(CO)_6]^+$ (in MeCN with 0.2 mol dm^{-3} $[NBu^n{}_4][BF_4]$ as base electrolyte[†]), and using equation (1), a value of P_L(NCS) = −1.03 V is deduced, very different from that (−0.88 V) in ref. 10. Using the modified value of P_L(NCS), the plot of E^0 *versus* P_L for (**1**), including the thiocyanate, has R = 0.998.

We now believe that the apparent variation in P_L for the thiocyanate ligand results from linkage isomerism. It is important to note that the value of P_L(NCS) given in ref. 10 was not taken directly from measurements on $[Cr(NCS)(CO)_5]^-$ but was extrapolated from data for the series of complexes $[MoL(CO)(dppe)_2]^z$, including, of course, the thiocyanate (z = −1).[14] The binding site $Mo(CO)(dppe)_2$ is considerably more electron-rich[10] than $Cr(CO)_5$ so that S-bonding by the thiocyanate ligand to molybdenum and N-bonding to chromium is entirely reasonable. We therefore propose that the P_L value of −0.88 V given in ref. 10 should be denoted P_L(SCN), and that deduced from studies on (**1**) (*i.e.* −1.03 V) should be designated P_L(NCS). In order to confirm this proposal we intend to carry out *X*-ray structural studies on appropriate salts of the anions $[Cr(NCS)(CO)_5]^-$ and $[Mo(SCN)(CO)(dppe)_2]^-$. It is noteworthy that such studies on *fac*-$[Mn(NCS)(CO)_3(dppm)]$ have confirmed the presence of the N-bonded isomer.[7]

Table 2. Infrared spectroscopic data[*] for *trans*-$[MnL(CO)(dppm)_2]^z$ (**2**) in CH_2Cl_2

L	z	ṽ(CO)/cm^{-1}	ṽ(CN)/cm^{-1}
CN	+1	1 941 (1 865)	
CO	+2	1 982 (1 915)	
CNMe	+2	1 969 (1 901)	2 196 (2 149)
CNBu^t	+2	1 970 (1 899)	2 184 (2 118)
NCMe	+2	1 944 (1 867)	

[*] Data for (**1**) are given in parentheses.

The plot of E^0 *vs.* P_L for (**1**) [using P_L(NCS) = −1.03 V] gives 0.86 V and 0.75 for E_s and β respectively. The E_s value, which is a measure of the electron-richness of the site $[Mn(CO)(dppm)_2]^+$, may be compared with other such values for closely related sites. Thus, for example, the species $MoL(dppe)_2$ (*e.g.*: L = CO, E_s = −0.11 V; L = N_2, E_s = −0.13 V; L = NCPh, E_s = −0.40 V)[10] have E_s values *ca.* 1 V more negative[‡] than that of the manganese cation, providing some quantification for the effect of a positive charge in isoelectronic series (and also underlining the differences in electron-richness referred to above in relation to the linkage isomerism in thiocyanates).

The β values for the various binding sites may also be compared, and here it is notable that there is little difference between $[Mn(CO)(dppm)_2]^+$ (0.75) and $Mo(CO)(dppe)_2$ (0.72). This comparison seems to support Pickett's conclusion[10] that the axial ligand of the square-pyramidal site is the prime cause of any variation in β. The charge appears to have little effect.

The Synthesis and Characterisation of trans-$[MnL(CO)(dppm)_2]^{z+1}$ (**2**).—The low E^0 values for the one-electron oxidation of (**1**), particularly of the neutral compounds, and the stability of the resulting manganese(II) derivatives when formed electrolytically, suggested that it should be possible to synthesise and isolate *trans*-$[MnL(CO)(dppm)_2]^{z+1}$ (**2**) by chemical methods. Accordingly, the reactions of (**1**) with oxidants such as $[NO]^+$, $[N_2C_6H_4F\text{-}p]^+$, and $[Fe(\eta-C_5H_5)_2]^+$ have been explored.

The complexes (**1**; z = 0, L = CN; z = +1, L = CO, CNMe, CNBu^t, or NCMe) react with excess $[NO][PF_6]$ (rapidly) or $[N_2C_6H_4F\text{-}p][PF_6]$ (more slowly) to give deep red or purple solutions each showing one i.r. carbonyl band (Table 2) approximately 65—75 cm^{-1} to higher energy than that of (**1**); the i.r. spectrum of (**2**; z = 0, L = NCS) was not detected. In two cases, the manganese(II) products were isolable; filtration of the reaction mixture and addition of n-hexane gave high yields of dark red (L = CNMe) or purple (L = CNBu^t) solids which analysed (C, H, and N) as $[MnL(CO)(dppm)_2][PF_6]_2$ (**2**; z = +1, L = CNMe or CNBu^t), the former as a CH_2Cl_2 solvate. Similar treatment of the solution formed by $[NO][PF_6]$ oxidation of (**1**; z = +1, L = NCMe) also gave a red-purple solid but slow decomposition prevented a satisfactory analysis;

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[*] R is the correlation coefficient, defined by: $R = [(\bar{x}.\bar{y}) - \bar{x}.\bar{y}]/\{[(\bar{x})^2 - (\overline{x^2})][(\bar{y})^2 - (\overline{y^2})]\}^{\frac{1}{2}}$.

[†] Under these conditions, E^0 for the couple $[Fe(\eta-C_5H_5)_2]^+$–$[Fe(\eta-C_5H_5)_2]$ is 0.41 V[14] (*cf.* 0.47 V in the present study).

[‡] A strict comparison is impossible in that the E_s values in ref. 10 are effectively *versus* the AgCl–Ag electrode in thf, *cf. versus* s.c.e. in CH_2Cl_2 in this work. This underlines the need for an internal standard such as ferrocene to be used when redox potentials are measured (as recommended by IUPAC[15]). Note that the β values may be directly compared; as defined by equation (2) they should not depend on the reference potential.

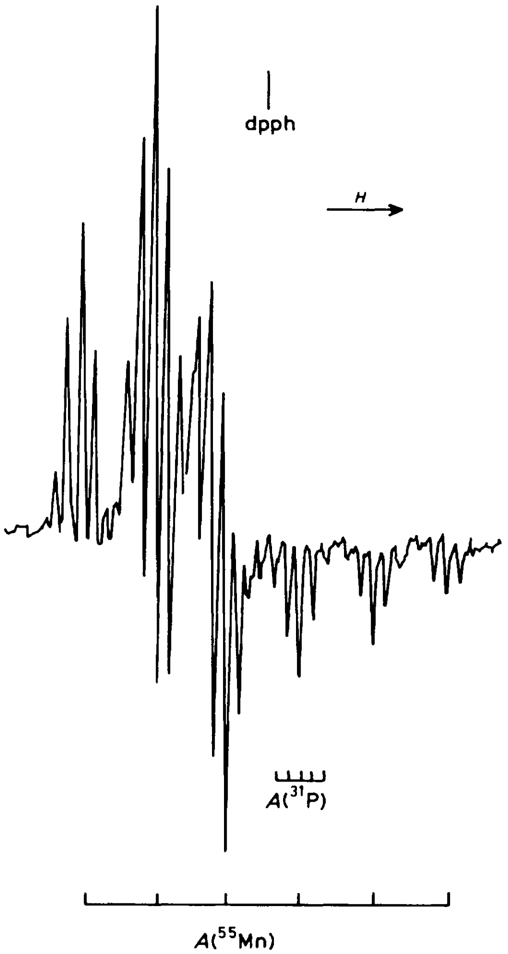

Figure. The e.s.r. spectrum of *trans*-$[Mn(CNBu^t)(CO)(dppm)_2]^{2+}$ in a CH_2Cl_2 thf (1:2) glass at −110 °C

insufficient quantities of (**1**; $z = 0$, L = CN or NCS) precluded oxidation on a preparative scale.

E.s.r. spectra have been obtained for all of the compounds (**2**; $z = 0$, L = CN or NCS; $z = +1$, L = NCMe, CNMe, or $CNBu^t$) confirming their paramagnetism, and also that the oxidation of (**1**) does not result in isomerisation.

At room temperature, the e.s.r. spectra are poorly defined; the six lines ($A \approx 100$ G) resulting from the coupling of the unpaired electron with the manganese atom (^{55}Mn, $I = \frac{5}{2}$) show some further coupling to the ^{31}P nuclei [$A(^{31}P) \approx 30$ G] but the broadness and irregularity of the spectra have prevented the accurate measurement of g and A values. At −110 °C, however, highly resolved spectra have been obtained in CH_2Cl_2–thf (1:2) glasses. The Figure shows one such spectrum, for (**2**; $z = +1$, L = $CNBu^t$). Although complex, it is clearly near-axial with the unique g-component showing coupling to manganese [$A(^{55}Mn) = 158$ G] and to four equivalent phosphorus atoms [$A(^{31}P) = 28$ G] (each of the six lines of this component is split into a 1:4:6:4:1 quintet). At a qualitative level, the spectra confirm that the paramagnetic species (**2**) retain the *trans* geometry of (**1**). However, a detailed analysis of these spectra, currently in progress,[16] should provide an invaluable insight into the bonding in octahedral manganese(II) carbonyl derivatives.

The Chemical and Electrochemical Oxidation of trans-$[MnBr(CO)(dppm)_2]$.—As noted above, the cyclic voltammogram of (**1**; $z = 0$, L = Br) suggested that (**2**; $z = 0$, L = Br) was far less stable than any other example of (**2**) and indeed controlled potential electrolysis at 0.05 V did not yield the manganese(II) cation. Surprisingly, however, the complete consumption of (**1**; $z = 0$, L = Br) required only 0.33 F mol^{-1}. The cyclic voltammogram of the product solution showed a new, reversible wave at $E^0 = 0.86$ V with a height approximately half that of (**1**; $z = 0$, L = Br) in the initial solution. The potential of this new wave corresponds exactly to that for the oxidation of (**1**; $z = 1$, L = CO) (Table 1) and the product solution showed one carbonyl band in the i.r. spectrum at 1 915 cm^{-1} (Table 2), as expected for *trans*-$[Mn(CO)_2(dppm)_2]^+$. No other electrolysis product could be identified either by i.r. spectroscopy or cyclic voltammetry although a small quantity of a white precipitate was observed in the electrochemical cell.

It is tempting to suggest that the oxidation of (**1**; $z = 0$, L = Br) is described by equations (3) and (4) although further supportive evidence is required; it should be noted that if these reactions were to occur, a value of $n = 0.5$ would be expected for the coulometric experiment.

$$trans\text{-}[MnBr(CO)(dppm)_2] \xrightleftharpoons{-e^-} trans\text{-}[MnBr(CO)(dppm)_2]^+ \quad (3)$$

$$\begin{array}{c} trans\text{-}[MnBr(CO)(dppm)_2] + trans\text{-}[MnBr(CO)(dppm)_2]^+ \\ \downarrow \\ trans\text{-}[Mn(CO)_2(dppm)_2]^+ + \text{‘}MnBr_2(dppm)_2\text{’} \end{array} \quad (4)$$

The chemical oxidation of (**1**; $z = 0$, L = Br) mirrors the electrolytic reaction in that $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ gave *trans*-$[Mn(CO)_2(dppm)_2][PF_6]$ as the only carbonyl-containing product, in 46% yield [or 92% based on the overall stoicheiometry given by equations (3) and (4)]; once again a white precipitate was formed as a minor by-product.

This reaction does not provide a useful alternative synthesis of the dicarbonyl cation. However, the ready loss of the bromide ligand suggested that oxidation of (**1**; $z = 0$, L = Br) in the presence of a donor ligand might provide a route to (**2**), as in equations (3) and (5).

$$trans\text{-}[MnBr(CO)(dppm)_2]^+ + L \longrightarrow trans\text{-}[MnL(CO)(dppm)_2]^{2+} + Br^- \quad (5)$$

Alternatively, noting that (**1**; $z = 0$, L = Br) is oxidised more readily than all of the other complexes listed in Table 1, catalytic formation of (**1**) might occur according to equations (3), (5), and (6).

$$\begin{array}{c} trans\text{-}[MnL(CO)(dppm)_2]^{2+} + trans\text{-}[MnBr(CO)(dppm)_2] \\ \upharpoonleft\downharpoonright \\ trans\text{-}[MnL(CO)(dppm)_2]^+ + trans\text{-}[MnBr(CO)(dppm)_2]^+ \end{array} \quad (6)$$

The reactions between (**1**; $z = 0$, L = Br) and NCMe or $CNBu^t$ in the presence of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ appear to bear out the second possibility. Thus, (**1**; $z = +1$, L = NCMe) has been prepared in 53% yield [and the $CNBu^t$ analogue in lesser quantities (28%)] using (**1**; $z = 0$, L = Br) and the ferrocenium ion in a ratio of *ca.* 3:1; the solid hexafluorophosphate salts are isolable on addition of $[NH_4][PF_6]$ to the reaction mixture.

The process can also be initiated electrolytically. Passing 0.33 F mol^{-1}, at 0.07 V, through a solution of (**1**; $z = 0$, L = Br) and CH_3CN in CH_2Cl_2 resulted in the complete consumption of the bromide complex (as measured by cyclic voltammetry) and the formation of diamagnetic (**1**; $z = +1$, L = NCMe). Voltammetry at the rotating platinum electrode verified that the product was in the reduced form [*i.e.* (**2**; $z = +1$, L = NCMe) was absent] with the wave height *ca.* 50% of that of (**1**; $z = 0$, L = Br) in the pre-electrolysed solution. Cyclic voltammetry also showed that *trans*-[Mn(CO)$_2$(dppm)$_2$][PF$_6$] was not a product of the reaction.

If the formation of (**1**; $z = +1$, L = NCMe) from (**1**; $z = 0$, L = Br) is catalytic, as described by equations (3), (5), and (6), the process does not appear to be very efficient (requiring 0.33 F mol^{-1} in the electrolysis or a 3:1 ratio of substrate to chemical oxidant). However, alternative mechanisms seem less likely. For example, the formation of *trans*-[Mn(CO)$_2$(dppm)$_2$]$^+$, as occurs in the absence of added ligand, followed by carbonyl substitution can be ruled out. The dicarbonyl cation only reacts with NCMe or CNBu^t to give [MnL(CO)(dppm)$_2$]$^+$ under u.v. irradiation.[17] Similarly, substitution of *trans*-[Mn(CO)$_2$(dppm)$_2$]$^{2+}$ is unlikely; neither the ferrocenium ion (E^0 = 0.47 V) nor the applied voltage (0.07 V) would generate significant quantities of the dication (E^0 = 0.86 V).

Experimental

The preparation, purification, and reactions of the complexes were carried out in flasks shielded from light by aluminium foil, and under an atmosphere of dry nitrogen; i.r. spectroscopy was used to monitor the course of the reactions. In general, products (*i*) were purified by dissolving in CH$_2$Cl$_2$, filtration, addition of n-hexane or diethyl ether, and partial evaporation of the solvent mixture *in vacuo* to induce precipitation, and (*ii*) are air-stable, dissolving in polar solvents such as CH$_2$Cl$_2$ or CH$_3$NO$_2$ to give moderately air-sensitive solutions. The compounds [MnL(CO)(dppm)$_2$] (L = Br, CN, or NCS),[7] [MnL(CO)(dppm)$_2$][PF$_6$] (L = CNMe,[7] CNBu^t,[8] NCMe,[8] or CO[9]), and [Fe(η-C$_5$H$_5$)$_2$][PF$_6$][18] were prepared by published methods. The salt [NO][PF$_6$] was purchased from Fluorochem Ltd. (Glossop, Derbyshire).

Infrared spectra were recorded on a Nicolet MX-5 FT spectrometer, or a Perkin-Elmer PE 257 spectrometer with calibration against the absorption band of polystyrene at 1 601 cm^{-1}. *X*-Band e.s.r. spectra were recorded on a Varian Associates 4502/15 instrument and were calibrated against a 10^{-4} mol dm^{-3} aqueous solution of K$_2$[NO(SO$_3$)$_2$] (5×10^{-2} mol dm^{-3} in K$_2$CO$_3$ as buffer) or a solid sample of the diphenylpicrylhydrazyl radical (dpph). Electrochemical studies were carried out using an AMEL Electrochemolab instrument in conjunction with a three-electrode cell. For cyclic voltammetry the working electrode was a platinum bead, the auxiliary electrode a platinum wire, and the reference an aqueous saturated calomel electrode (s.c.e.) separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. A similar configuration was used for controlled potential electrolysis but with a platinum gauze basket as the working electrode and a platinum spiral as auxiliary electrode. Voltammetry used the platinum bead electrode rotated at 600 revolutions min^{-1}. Solutions were 0.5×10^{-3} and 1.0×10^{-3} mol dm^{-3} in complex for voltammetry and controlled potential electrolysis respectively; in both cases the solutions were 0.1 mol dm^{-3} in [NBu$^n{}_4$][PF$_6$] as supporting electrolyte. Under these conditions, E^0 for the couples [Fe(η-C$_5$H$_5$)$_2$]$^+$–[Fe(η-C$_5$H$_5$)$_2$] and [Fe(η-C$_5$Me$_5$)$_2$]$^+$–[Fe(η-C$_5$Me$_5$)$_2$] are 0.47 and −0.07 V respectively. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

trans-*Bis*[*bis*(*diphenylphosphino*)*methane*]*carbonyl*(*t-butyl isocyanide*)*manganese*(II) *Bis*(*hexafluorophosphate*)–*Dichloromethane* (1/1), *trans*-[Mn(CO)(CNBu^t)(dppm)$_2$][PF$_6$]$_2$·CH$_2$Cl$_2$.—To a stirred solution of [Mn(CO)(CNBu^t)(dppm)$_2$][PF$_6$] (0.15 g, 0.14 mmol) in CH$_2$Cl$_2$ (40 cm^3) was added solid [NO][PF$_6$] (0.1 g, 0.33 mmol). After 20 min the purple solution was filtered and hexane (60 cm^3) was added to precipitate the product. Purification from CH$_2$Cl$_2$–diethyl ether, followed by washing with toluene, gave a crimson-purple solid, yield 0.13 g (76%) (Found: C, 51.9; H, 4.2; N, 1.5. C$_{57}$H$_{55}$Cl$_2$F$_{12}$MnNOP$_6$ requires C, 52.3; H, 4.2; N, 1.1%).

The complex [Mn(CO)(CNMe)(dppm)$_2$][PF$_6$]$_2$ was similarly prepared as dark red crystals in 94% yield. It is only sparingly soluble in CH$_2$Cl$_2$ and was therefore purified from nitromethane–diethyl ether (Found: C, 52.8; H, 3.9; N, 1.2. C$_{53}$H$_{47}$F$_{12}$MnNOP$_6$ requires C, 53.8; H, 4.0; N, 1.2%).

trans-*Bis*[*bis*(*diphenylphosphino*)*methane*]*dicarbonylmanganese*(I) *Hexafluorophosphate*, *trans*-[Mn(CO)$_2$(dppm)$_2$][PF$_6$].—To a stirred solution of *trans*-[MnBr(CO)(dppm)$_2$] (0.20 g, 0.22 mmol) was added [Fe(η-C$_5$H$_5$)$_2$][PF$_6$] (0.02 g, 0.07 mmol). After 15 min the yellow solution was filtered, to remove a small amount of a white precipitate, and then evaporated to dryness. The residue was then dissolved in acetone (20 cm^3), a solution of [NH$_4$][PF$_6$] (0.04 g, 0.22 mol) in acetone (15 cm^3) was added, and the reaction mixture was filtered. Addition of n-hexane (60 cm^3) and partial evaporation of the solvent *in vacuo* gave a yellow precipitate which was purified from CH$_2$Cl$_2$–n-hexane to give the product as a yellow solid, yield 0.10 g (46%, based on manganese).

trans-*Acetonitrilebis*[*bis*(*diphenylphosphino*)*methane*]*carbonylmanganese*(I) *Hexafluorophosphate*, *trans*-[Mn(CO)(NCMe)(dppm)$_2$][PF$_6$].—To *trans*-[MnBr(CO)(dppm)$_2$] (0.20 g, 0.22 mmol) and acetonitrile (1 cm^3) in CH$_2$Cl$_2$ (20 cm^3) was added [Fe(η-C$_5$H$_5$)$_2$][PF$_6$] (0.024 g, 0.07 mmol). After stirring for 30 min, the solution was filtered and then evaporated to dryness. The residue was then dissolved in acetone (30 cm^3) and [NH$_4$][PF$_6$] (0.04 g, 0.22 mmol) in acetone (20 cm^3) was added. Filtration, addition of n-hexane (*ca.* 60 cm^3), and partial evaporation to dryness gave an orange solid which was purified from dichloromethane–n-hexane to give the product as an orange solid, yield 0.12 g (53%).

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