# Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 5.[1] The One-electron Oxidation of Tricarbonyl(η-cyclopentadienyl)-manganese Derivatives and the Reactivity of the resulting Radical Cations

By **Neil G. Connelly*** and **Maureen D. Kitchen**, Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS

Cyclic-voltammetric studies in $CH_2Cl_2$ have shown that $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)_{3-x}L_x]$ [$n$ = 0, 1, or 5, $x$ = 1, L = phosphine or phosphite (1); $n$ = 0 or 1, $x$ = 2, L = ½dppe (dppe = $Ph_2PCH_2CH_2PPh_2$), $PPh_3$, or $PMePh_2$] each undergo a reversible one-electron oxidation to $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)_{3-x}L_x]^+$ [$x$ = 1 (3) or 2 (4)]. The paramagnetic cations (3) may be generated chemically by silver(I) ion oxidation of (1), and (4) may be isolated from either silver(I) ion or diazonium ion oxidation of (2). On reaction with $[N(C_6H_4Br\text{-}p)_3][SbCl_6]$, $SbCl_5$, $Br_2$, or $I_2$, (1) and (2) afford the diamagnetic complexes $[MnX(\eta\text{-}C_5H_{5-n}Me_n)(CO)_{3-x}L_x]^+$ [X = Cl, Br, or I, $x$ = 1 (5) or 2 (6)], *via* the attack of halogen radicals on (3) or (4). The relation between the oxidation potential, $E_p$, and $k$(CO), the force constant for the carbonyl-stretching vibrations, for (1), (2), and $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)_3]$ is discussed with reference to that previously reported for the isoelectronic chromium complexes $[Cr(\eta\text{-}C_6Me_6)(CO)_2L]$.

We have previously shown[2] that the complexes $[Cr(\eta\text{-}C_6Me_6)(CO)_2L]$ (L = phosphine or phosphite) undergo reversible one-electron oxidation reactions and that there is a linear relation between $\bar{\nu}$(CO) (av.) and $E_p$, the potential at which the oxidation occurs. On the basis of this relation we suggested that the simple measurement of i.r. carbonyl-stretching frequencies might be useful in the direct prediction of the $E_p$ values (and therefore of the redox chemistry) of carbonyl complexes isoelectronic with $[Cr(\eta\text{-}C_6Me_6)(CO)_2L]$. Preliminary studies[2] revealed a good agreement between the measured values of $E_p$ for $[Mn(\eta\text{-}C_5H_4Me)(CO)_2L]$ [L = $P(OPh)_3$, $PPh_3$, or $PEt_3$] and those calculated using the relation between $E_p$ and $\bar{\nu}$(CO) (av.) for $[Cr(\eta\text{-}C_6Me_6)(CO)_2L]$. We have now found, however, by investigating a large number of tricarbonyl(η-cyclopentadienyl)-manganese derivatives $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)_{3-x}L_x]$ [$x$ = 1 (1) or 2 (2)], that there is a direct relation between

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[1] Part 4, N. G. Connelly and R. L. Kelly, *J. Organometallic Chem.*, 1976, **120**, C16.

[2] N. G. Connelly, Z. Demidowicz, and R. L. Kelly, *J.C.S. Dalton*, 1975, 2335.

oxidation potential and carbonyl-stretching frequency for these species but that it does not correspond exactly to that for the chromium complexes. In addition we have shown that the paramagnetic cations $[\mathrm{Mn}(\eta\text{-}\mathrm{C_5H_{5-\mathit{n}}Me_\mathit{n}})(\mathrm{CO})_{3-x}\mathrm{L}_x]^+$ [$x = 1$ (3) or 2 (4)], preliminary studies on some of which have recently been reported by other workers,[3-5] may be generated chemically and that they are intermediates in the formation of the diamagnetic halogeno-complexes $[\mathrm{MnX}(\eta\text{-}\mathrm{C_5H_{5-\mathit{n}}Me_\mathit{n}})(\mathrm{CO})_{3-x}\mathrm{L}_x]^+$ [X = Cl, Br, or I, $x = 1$ (5) or 2 (6)] from (1) or (2) and $[\mathrm{N(C_6H_4Br\text{-}\mathit{p})_3}][\mathrm{SbCl_6}]$, $\mathrm{SbCl_5}$, $\mathrm{Br_2}$, or $\mathrm{I_2}$.

## RESULTS AND DISCUSSION

*Electrochemical Studies.*—Complexes (1) and (2) were prepared by modifications of published methods (see Experimental section) and were characterised fully before use (Table 1). Cyclic-voltammetric studies in $\mathrm{CH_2Cl_2}$ showed that each complex underwent only one redox process (in the range ±1.5 V) at the stationary platinum-wire electrode; unlike other workers,[4,5] we did not detect more than one oxidation step. A comparison of the values of $(E_\mathrm{p})_\mathrm{ox} - (E_\mathrm{p})_\mathrm{red}$, $(i_\mathrm{p})_\mathrm{ox}$, and $(i_\mathrm{p})_\mathrm{red}$ (Table 2) for (1) and (2) with those for the electron-transfer process $[\mathrm{Ni\{S_2C_2(CN)_2\}_2}]^{2-} \rightleftharpoons [\mathrm{Ni\{S_2C_2(CN)_2\}_2}]^-$ confirmed that in all the cases (1) and (2) are oxidised in a reversible one-electron step, to $[\mathrm{Mn}(\eta\text{-}\mathrm{C_5H_{5-\mathit{n}}Me_\mathit{n}})$-

TABLE 1

Analytical and m.p. data for $[\mathrm{Mn}(\eta\text{-}\mathrm{C_5H_{5-\mathit{n}}Me_\mathit{n}})(\mathrm{CO})_2\mathrm{L}]$ (1) and $[\mathrm{Mn}(\eta\text{-}\mathrm{C_5H_{5-\mathit{n}}Me_\mathit{n}})(\mathrm{CO})\mathrm{L}_2]$ (2)

| Complex | L | *n* | Colour | M.p. (θc/°C) | Yield (%) | *M* [a] | Analysis (%) [b] C | H |
|---|---|---|---|---|---|---|---|---|
| (1) | $\mathrm{P(OPh)_3}$ | 0 | Yellow | 116—118 | 45 | 486 | 61.5 (61.7) | 4.4 (4.2) |
| | $\mathrm{PPh_3}$ | 0 | Yellow | 162—164 | 52 | 438 | 68.3 (68.5) | 4.6 (4.6) |
| | $\mathrm{PEt_3}$ | 0 | Yellow oil | | 43 | 294 | 53.3 (53.1) | 7.0 (6.9) |
| | $\mathrm{P(OPh)_3}$ | 1 | Yellow | 78—80 | 73 | 500 | 62.9 (62.7) | 4.6 (4.5) |
| | $\mathrm{P(OMe)_3}$ | 1 | Yellow oil | | 32 | 314 | 42.7 (42.1) | 5.5 (5.1) |
| | $\mathrm{PPh_3}$ | 1 | Yellow | 119—120 | 44 | 452 | 68.6 (69.0) | 4.8 (4.9) |
| | $\mathrm{PMe_2Ph}$ | 1 | Yellow | 60—63 | 27 | 328 | 58.5 (58.5) | 5.7 (5.5) |
| | $\mathrm{PEt_3}$ | 1 | Yellow oil | | 33 | 308 | 55.2 (54.6) | 7.6 (7.2) |
| | $\mathrm{PPh_3}$ | 5 | Yellow | Decomp. >165 | 48 | 508 | 71.0 (70.9) | 6.0 (6.0) |
| (2) | $\mathrm{PPh_3}$ | 0 | Red | Decomp. >149 | 24 | | 74.5 (75.0) | 5.3 (5.3) |
| | $\mathrm{PPh_3}$ | 1 | Red | Decomp. >133 | 87 | | 75.4 (75.2) | 5.6 (5.3) |
| | $\mathrm{PMePh_2}$ | 1 | Orange | Decomp. >130 | 61 | | 70.2 (70.5) | 6.0 (5.9) |
| | ½dppe | 1 | Orange | 149—151 | 42 | | 70.4 (70.7) | 5.6 (5.8) |

[a] By mass spectrometry. [b] Calculated values are given in parentheses.

TABLE 2

I.r. and electrochemical data [a] for $[\mathrm{Mn}(\eta\text{-}\mathrm{C_5H_{5-\mathit{n}}Me_\mathit{n}})(\mathrm{CO})_2\mathrm{L}]^z$ [$z = 0$ (1) or 1 (3)] and $[\mathrm{Mn}(\eta\text{-}\mathrm{C_5H_{5-\mathit{n}}Me_\mathit{n}})(\mathrm{CO})\mathrm{L}_2]^z$ [$z = 0$ (2) or 1 (4)]

| Complex | L | *n* | *z* | $\bar{\nu}$(CO) [b] cm$^{-1}$ | *k* mdyn Å$^{-1}$ | $E_\mathrm{p}$ [c] V | $(E_\mathrm{p})_\mathrm{ox} - (E_\mathrm{p})_\mathrm{red}$ [d] mV | $(i_\mathrm{p})_\mathrm{ox}$ [d] µA | $(i_\mathrm{p})_\mathrm{red}$ [d] µA |
|---|---|---|---|---|---|---|---|---|---|
| (1) | $\mathrm{P(OPh)_3}$ | 0 | 0 | 1 961, 1 893 | 15.00 | 0.92 | 150 | 3.7 | 3.6 |
| | $\mathrm{PPh_3}$ | 0 | 0 | 1 931, 1 863 | 14.54 | 0.59 | 145 | 3.1 | 2.9 |
| (3) | $\mathrm{PPh_3}$ | 0 | 1 [e] | 2 045, 1 965 | | | | | |
| (1) | $\mathrm{PEt_3}$ | 0 | 0 | 1 922, 1 851 | 14.38 | 0.49 | 170 | 5.2 | 4.8 |
| (3) | $\mathrm{PEt_3}$ | 0 | 1 | 2 037, 1 951 | | | | | |
| (1) | $\mathrm{P(OPh)_3}$ | 1 | 0 | 1 957, 1 891 | 14.95 | 0.88 | 140 | 3.5 | 3.2 |
| (3) | $\mathrm{P(OPh)_3}$ | 1 | 1 [e] | 2 053, 1 981 | | | | | |
| (1) | $\mathrm{P(OMe)_3}$ | 1 | 0 | 1 944, 1 874 | 14.72 | 0.73 | 160 | 4.2 | 3.9 |
| | $\mathrm{PPh_3}$ | 1 | 0 | 1 927, 1 861 | 14.49 | 0.57 | 160 | 3.9 | 3.6 |
| (3) | $\mathrm{PPh_3}$ | 1 | 1 | 2 041, 1 961 | | | | | |
| (1) | $\mathrm{PMe_2Ph}$ | 1 | 0 | 1 923, 1 852 | 14.39 | 0.50 | 160 | 4.6 | 4.2 |
| (3) | $\mathrm{PMe_2Ph}$ | 1 | 1 | 2 039, 1 953 | | | | | |
| (1) | $\mathrm{PEt_3}$ | 1 | 0 | 1 919, 1 845 | 14.33 | 0.45 | 160 | 4.8 | 5.0 |
| (3) | $\mathrm{PEt_3}$ | 1 | 1 | 2 029, 1 945 | | | | | |
| (1) | $\mathrm{PPh_3}$ | 5 | 0 | 1 915, 1 845 | 14.27 | 0.37 | 140 | 2.4 | 2.6 |
| (2) | $\mathrm{PPh_3}$ | 0 | 0 | 1 824 | 13.44 | −0.21 | 140 | 2.4 | 2.4 |
| (4) | $\mathrm{PPh_3}$ | 0 | 1 [f] | 1 918 | | | | | |
| (2) | $\mathrm{PPh_3}$ | 1 | 0 | 1 816 | 13.32 | −0.27 | 130 | 1.5 | 1.5 |
| (4) | $\mathrm{PPh_3}$ | 1 | 1 [f] | 1 913 | | | | | |
| (2) | $\mathrm{PMePh_2}$ | 1 | 0 | 1 815 | 13.30 | −0.28 | 140 | 2.5 | 2.5 |
| (4) | $\mathrm{PMePh_2}$ | 1 | 1 [f] | 1 912 | | | | | |
| (2) | ½dppe | 1 | 0 | 1 826 | 13.47 | −0.16 | 155 | 3.7 | 3.9 |
| (4) | ½dppe | 1 | 1 | 1 926 | | −0.17 | 130 | 1.5 | 1.5 |

[a] For the reversible one-electron oxidation of $[\mathrm{Ni\{S_2C_2(CN)_2\}_2}]^{2-}$ : $(E_\mathrm{p})_\mathrm{ox} - (E_\mathrm{p})_\mathrm{red} = 140$ mV; $(i_\mathrm{p})_\mathrm{ox} = 3.0$ µA; $(i_\mathrm{p})_\mathrm{red} = 2.9$ µA. [b] In $\mathrm{CH_2Cl_2}$. [c] Relative to a calomel electrode (1 mol dm$^{-3}$ in LiCl). [d] Values for scan rate of 100 mV s$^{-1}$. [e] Generated in $\mathrm{CH_2Cl_2}$ by addition of $\mathrm{Ag[BF_4]}$. [f] Generated in $\mathrm{CH_2Cl_2}$ by addition of $[\mathrm{PhN_2}][\mathrm{PF_6}]$.

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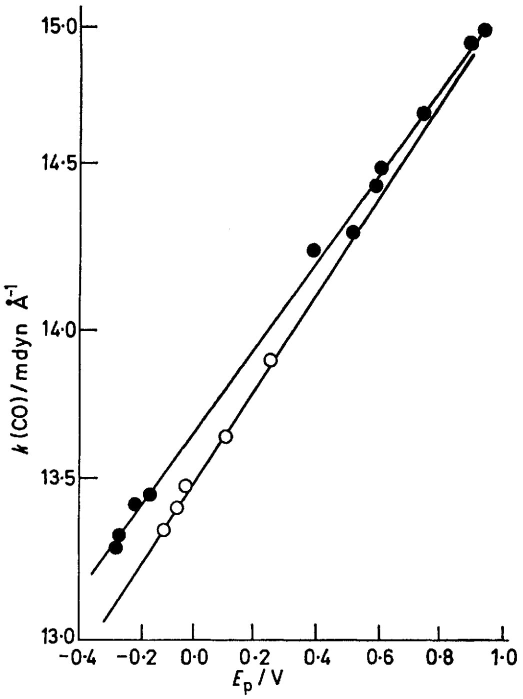
[3] P. M. Treichel, K. P. Wagner, and H. J. Mueh, *J. Organometallic Chem.*, 1975, **86**, C13.

[4] L. I. Denisovich, N. V. Zakurin, S. P. Gubin, and A. G. Ginzburg, *J. Organometallic Chem.*, 1975, **101**, C43.

[5] C. J. Pickett and D. Pletcher, *J.C.S. Dalton*, 1976, **636**.

$(CO)_{3-x}L_x]^+$ [$x = 1$ (3) or 2 (4)].* The potential, $E_p$, at which oxidation occurred varied from −0.28 to +0.92 V and depended on the nature of L, $x$, and $n$. It is most dependent on $x$ so that, for example, substitution of a second carbonyl group in (1; $n = 0$, L = $PPh_3$) by $PPh_3$ to give (2; $n = 0$, L = $PPh_3$) resulted in a shift of $E_p$ to more negative potentials by *ca.* 0.8 V. The dependence of $E_p$ on $n$ and L is as expected with an increase in $n$ or in the donor ability of L causing $E_p$ to become more negative. The data shown in Table 2 suggest that $E_p$ is shifted by *ca.* 40 mV to more negative potentials for each extra methyl group on the cyclopentadienyl ring.



Plot of $k$(CO) against $E_p$ for $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)_{3-x}L_x]$ (●) and $[Cr(\eta\text{-}C_6Me_6)(CO)_2L]$ (O) [2] in $CH_2Cl_2$

A plot of $\bar{\nu}$(CO) (av.) against $E_p$ for (1) is linear. It is more useful, however, to relate $E_p$ to $k$(CO), the force constant for the carbonyl-stretching frequencies of (1) and (2). The Figure shows the relation between $E_p$ and $k$(CO), calculated by the Cotton–Kraihanzel method,[6] for (1) and (2) and for $[Cr(\eta\text{-}C_6Me_6)(CO)_2L]$. The assumption of octahedral geometry for the complexes in the calculation of $k$(CO) seems valid on the basis of the known molecular structures of $[Mn(\eta\text{-}C_5H_5)(CO)_2(PPh_3)]$ [7] and $[Cr(\eta\text{-}C_6Me_6)(CO)_2(PPh_3)]$.[8] It is clear, by fitting the data to straight lines by least-squares methods, that the relation between $E_p$ and $k$(CO) for the manganese complexes does not quite coincide with that for the chromium complexes. The gradients and intercepts ($E_p$ 0.0 V) for the manganese and chromium data (with standard deviations in parentheses) are 1.40 (0.02) and 1.55 (0.08) mdyn Å$^{-1}$ V$^{-1}$, and 13.71 (0.01) and 13.55 (0.01) mdyn Å$^{-1}$ respectively.† Thus, although $E_p$ values can be predicted from force-constant data for closely related species, extrapolation to other series of complexes is of limited value.

The use of force-constant data rather than the average value for the carbonyl-stretching frequencies is illustrated by considering the electrochemical and i.r.-spectral results for the parent tricarbonyls $[Cr(\eta\text{-}C_6Me_6)(CO)_3]$ and $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)_3]$ ($n = 0$, 1, or 5). Although poor agreement between the data for $[Cr(\eta\text{-}C_6Me_6)(CO)_3]$ and for $[Cr(\eta\text{-}C_6Me_6)(CO)_2L]$ (L = phosphine or phosphite) was found when using $\bar{\nu}$(CO) (av.), good agreement resulted by using $k$(CO) values. The linear plot of $E_p$ against $k$(CO) for the manganese complexes includes data both for $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)_2L]$ (1) and for $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)L_2]$ (2). It seems reasonable to assume, therefore, that the plot is also valid for the parent tricarbonyls. The $E_p$ values of $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)_3]$ may therefore be estimated as 1.33 [$n = 0$, $k$(CO) 15.57], 1.30 [$n = 1$, $k$(CO) 15.52], and 1.24 V [$n = 5$, $k$(CO) 15.44 mdyn Å$^{-1}$]. It is interesting to note that a linear relation has been found between $E_p$ and $x$ for $[Mn(CNMe)_x(CO)_{6-x}]^+$ and for $[Cr(CNMe)_x(CO)_{6-x}]$.[9-11] If such a relation holds for the manganese complexes reported here then an estimation of $E_p$ for $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)_3]$ ($n = 0$ and 1) may be made from the oxidation potentials measured for $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)_{3-x}(PPh_3)_x]$ ($n = 0$ or 1, $x = 1$ or 2). Accordingly $E_p$ values of 1.39 ($n = 0$) and 1.41 V ($n = 1$) may be estimated, in fair agreement with those found from the relation between $E_p$ and $k$(CO). Although we have been unable to study satisfactorily the electrochemical properties of $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)_3]$ in $CH_2Cl_2$, the reversible oxidation of the cyclopentadienyl complex ($n = 0$) has been observed [3] in $CF_3CO_2H$ [$E_p$ 0.79 *versus* standard calomel electrode (s.c.e.)].

*Synthetic Studies.*—The potentials, $E_p$, at which (1) and, more particularly, (2) are oxidised suggest that chemical oxidation of these species should be possible. The use of a wide range of oxidising agents has realised this possibility.

In $CH_2Cl_2$, (1) reacted with $[NO][PF_6]$ to give a

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* For each complex the value of $(i_p)_{ox}/(i_p)_{red}$ is close to unity, as required for a reversible electron-transfer process. The variation of $(i_p)_{ox}$ [or $(i_p)_{red}$] from complex to complex most likely results from slow decomposition in solution. For a given complex $(E_p)_{ox} - (E_p)_{red}$ varies with the scan rate, as expected, but for rates of 200, 100, and 50 mV s$^{-1}$ the value of $[(E_p)_{ox} + (E_p)_{red}]/2$ ($=E_p$) is invariant.

† Throughout this paper: 1 mdyn = $10^{-8}$ N; 1 G = $10^{-4}$ T.

[6] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4482.

[7] C. Barbeau, K. S. Dickmann, and L. Ricard, *Canad. J. Chem.*, 1973, **51**, 3073.

[8] B. A. Kelly, unpublished work.

[9] J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd, and J. A. McCleverty, *J.C.S. Dalton*, 1972, 1246.

[10] P. M. Treichel, G. E. Dureen, and H. J. Mueh, *J. Organometallic Chem.*, 1972, **44**, 339.

[11] C. J. Pickett and D. Pletcher, *J. Organometallic Chem.*, 1975, **102**, 327.

mixture of the known[12] nitrosyl complexes $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)_2(NO)]^+$ and $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)(NO)L]^+$ by displacement of L or CO. For (1; L = $PPh_3$, $n = 5$) preferential displacement of L occurred to give $[Mn(\eta\text{-}C_5Me_5)(CO)_2(NO)]^+$ only.[13] No attempts were made to isolate the nitrosyl complexes which were identified by comparing their i.r. spectra with those published. With (2), $[NO][PF_6]$ in $CH_2Cl_2$ afforded mixtures of the nitrosyl complexes $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)(NO)L]^+$ and the paramagnetic cations (4). The observation of both oxidation and substitution of (2) contrasts with the behaviour of $[Cr(\eta\text{-}C_6Me_6)(CO)_2L]$ for which only substitution occurs.[2]

No identifiable products resulted from the reaction of (1) with $[PhN_2][PF_6]$, either in $CH_2Cl_2$ or in acetone. With [2; L = $\frac{1}{2}Ph_2PCH_2CH_2PPh_2$ (dppe), $n = 1$], however, ready oxidation occurred to give (4) exclusively and addition of hexane to the reaction mixture gave orange crystals of $[Mn(\eta\text{-}C_5H_4Me)(CO)(dppe)][PF_6]$. Although an analytically pure sample of this salt could not be obtained, its identity was confirmed by cyclic voltammetry (Table 2), which showed one reduction wave at a potential of −0.17 V [identical, within experimental error, to that found for the oxidation of (2; L = $\frac{1}{2}$dppe, $n = 1$)], and by i.r. spectroscopy (Table 2) which showed an increase in $\bar{\nu}$(CO) of *ca.* 100 cm$^{-1}$ on oxidation of (2) to (4). The oxidation of other complexes of type (2; L = $PPh_3$ or $PMePh_2$, $n = 1$) could also be brought about by $[PhN_2][PF_6]$ in $CH_2Cl_2$ but the resulting cations were not isolated as stable solids. They, and (4; L = $\frac{1}{2}$dppe, $n = 1$) were, however, characterised by their solution e.s.r. spectra (see below).

Our previous studies[2] with $[Cr(\eta\text{-}C_6Me_6)(CO)_2L]$ allowed us to estimate $E(NO^+)$ and $E(PhN_2^+)$, the potentials at which the nitrosonium and benzenediazonium ions respectively would preferentially oxidise, rather than substitute, organotransition-metal carbonyls. We suggested, however, that these potentials might well vary from one series of substrates to another, particularly with a change in the central metal atom. Consideration of the electrochemical data for (1) and (2), together with the results of synthetic studies outlined above, shows that $-0.16 < E_{Mn}(PhN_2^+) < 0.37$ V. This does not allow us to say whether there is a dependence of $E(PhN_2^+)$ on the metal atom. That both substitution and oxidation of (2) with $NO^+$ occurs suggests that $E_{Mn}(NO^+)$ is in the region of −0.16 to −0.28 V, in agreement with the finding[2] of $-0.22 < E_{Cr}(NO^+) < -0.11$ V.

Although neither $[NO]^+$ nor $[PhN_2]^+$ oxidised the dicarbonyls (1) to (3), the addition of $Ag[BF_4]$ to (1) in $CH_2Cl_2$ resulted in an immediate colour change from pale yellow to dark red or purple. A similar colour change has been noted on formation of $[Mn(\eta\text{-}C_5H_5)(CO)_3]^+$ from $[Mn(\eta\text{-}C_5H_5)(CO)_3]$ by controlled-potential electrolysis.[5] The i.r. spectra (Table 2) of the reaction mixtures each showed two bands in the carbonyl-stretching region, shifted to higher wavenumbers by 100—120 cm$^{-1}$ from the values for (1), as expected for the formation of (3). Similar changes in the i.r. spectra of $[Cr(\eta\text{-}C_6Me_6)(CO)_2L]$ have been found[2] on oxidation to the monocations $[Cr(\eta\text{-}C_6Me_6)(CO)_2L]^+$. The cations (3) are too unstable to isolate, as might be expected from the values of $E_p$ for the oxidation of (1) (Table 2), and in the absence of excess of silver(I) ion rapid reduction of (3) to (1) occurs. Because of this instability and the need for the presence of excess of $Ag^+$, we were unable to record the e.s.r. spectra of (3). Addition of $Ag[PF_6]$ to (2; $n = 1$, L = $\frac{1}{2}$dppe, $PPh_3$, or $PMePh_2$) in $CH_2Cl_2$ again afforded the corresponding monocations (4), identical to those species resulting from oxidation of (2) by $[PhN_2][PF_6]$.

Triarylammonio-salts have been used in the oxidation of organic substrates[14] and have found limited use as oxidants in organometallic chemistry.[15] The reaction of $[N(C_6H_4Br\text{-}p)_3][SbCl_6]$ with (2; $n = 1$, L = $\frac{1}{2}$dppe) in $CH_2Cl_2$ resulted initially in the formation of (4), which could be isolated as orange crystals on the addition of hexane to the reaction mixture. Although microanalytical results (see Experimental section) were obtained which suggest the formation of (4) as its hexachloroantimonate salt, complete oxidation of (2) to (4) was brought about by using only 2 : 1 mol ratios of (2) to the ammonio-salt. It is noteworthy that both the cation $[N(C_6H_4Br\text{-}p)_3]^+$ and the anion $[SbCl_6]^-$ can function as oxidising agents and studies[16] with the latter ion have shown that the products formed may include $[SbCl_4]^-$, $[Sb_2Cl_9]^{3-}$, or $[SbCl_6]^{3-}$ as the counter anion. We feel, therefore, that the counter anion present in the product of the oxidation of (2; $n = 1$, L = $\frac{1}{2}$dppe) by $[N(C_6H_4Br\text{-}p)_3][SbCl_6]$ may not be $[SbCl_6]^-$. The addition of greater quantities of $[N(C_6H_4Br\text{-}p)_3][SbCl_6]$ resulted in further reaction of (4) to give deep red solutions, in $CH_2Cl_2$, which showed one carbonyl absorption at higher wavenumber than that due to (4). Although the complex is far too unstable to isolate for complete characterisation, we formulate it as $[MnCl(\eta\text{-}C_5H_4Me)(CO)(dppe)]^+$ on the basis of the following results. The reaction of $[N(C_6H_4Br\text{-}p)_3][SbCl_6]$ with (1) gave very deep red solutions which exhibited two carbonyl absorptions at higher wavenumber than those of (3) (Table 3). In order to determine whether incorporation of halogen occurred we treated (1) and (2) with $Br_2$ and $I_2$. In most cases deep red complexes of the type $[MnX(\eta\text{-}C_5H_{5-n}Me_n)(CO)_2L]^+$ (5) or $[MnX(\eta\text{-}C_5H_{5-n}Me_n)(CO)L_2]^+$ (6) were formed in $CH_2Cl_2$ solution. In only one case, however, were we able to isolate, and partially characterise the product. Addition of excess of iodine (5 : 1 mol ratio) to (1; $n = 1$, L = $PMe_2Ph$) in acetone followed by addition of diethyl ether yielded an unstable red oil which was dried

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*in vacuo* and analysed (C and H only) for [MnI($\eta$-$C_5H_4Me$)$(CO)_2$($PMe_2Ph$)][$I_9$]. Based on this formula, the measured conductivity ($\Lambda$ 150 S $cm^2$ $mol^{-1}$; $10^{-4}$ mol $dm^{-3}$ in acetone under nitrogen) is in good agreement with that expected for a 1 : 1 electrolyte. That (5) and (6) are halogeno-complexes is established by their i.r. spectra in the carbonyl region (Table 3). For (5) it is clear that varying any one of X, L, or *n* results in a shift of $\bar{\nu}$(CO), confirming the presence of the halogen, the cyclopentadienyl ring, and the ligand L. In addition a comparison of the values of $\bar{\nu}$(CO) for (5) with those of the isoelectronic neutral complexes [MoX($\eta$-$C_5H_5$)-$(CO)_2$L] [17] shows the expected shift to higher frequency for cations (5). It is interesting to note that both *cis* and *trans* isomers of [MoX($\eta$-$C_5H_5$)$(CO)_2$L] exist. A consideration of the relative intensities of the two carbonyl absorptions for (5) suggests that the *trans* isomer occurs in all cases except that in which X = Cl, L = $P(OPh)_3$, and *n* = 1. The intercarbonyl angles (2θ) for (5) have been estimated using the relation [18] $R_{sym}/R_{asym} = \cot^2\theta$, where $R_{sym}$ and $R_{asym}$ refer to the integrated intensities of the absorptions due to the symmetric and asymmetric stretching modes of the dicarbonyl unit. The variation of 2θ with X, L, and *n* in (5) is as expected on steric grounds, although the observation of the *cis* geometry for only [MnCl($\eta$-$C_5H_4Me$)$(CO)_2${P(OPh)$_3$}]$^+$ is somewhat surprising.

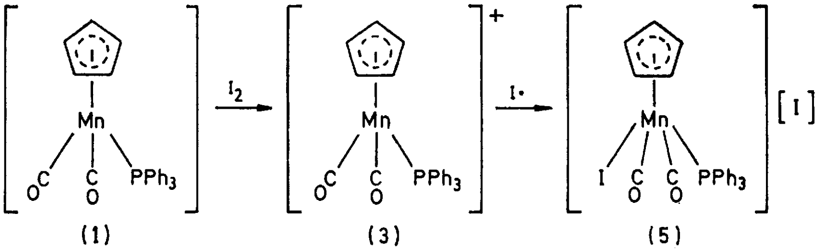
TABLE 3

I.r. data [a] for [MnX($\eta$-$C_5H_{5-n}Me_n$)$(CO)_2$L]$^+$ (5) and [MnX($\eta$-$C_5H_{5-n}Me_n$)(CO)$L_2$]$^+$ (6)

| Complex | X | L | *n* | $\bar{\nu}$(CO)/cm$^{-1}$ | $R_{sym}/R_{asym}$ [b] | 2θ [c]/° |
|---|---|---|---|---|---|---|
| (5) | I | $PPh_3$ | 0 | 2 045, 2 008 | 0.213 | 133.72 |
| | Cl | $P(OPh)_3$ | 1 | 2 082, 2 033 | 1.068 | 58.95 |
| | Br | $P(OPh)_3$ | 1 | 2 069, 2 033 | 0.887 | 105.35 |
| | Cl | $PPh_3$ | 1 | 2 067, 2 029 | 0.967 | 102.65 |
| | Br | $PPh_3$ | 1 | 2 057, 2 018 | 0.465 | 122.17 |
| | I | $PPh_3$ | 1 | 2 038, 2 000 | 0.335 | 128.20 |
| | Cl | $PMe_2Ph$ | 1 | 2 064, 2 005 | 0.840 | 106.93 |
| | Br | $PMe_2Ph$ | 1 | 2 052, 2 012 | 0.430 | 123.50 |
| | I | $PMe_2Ph$ | 1 | 2 037, 1 996 | 0.471 | 121.85 |
| | Cl | $PEt_3$ | 1 | 2 065, 2 001 | 0.984 | 102.15 |
| | Br | $PEt_3$ | 1 | 2 049, 2 007 | 0.689 | 126.30 |
| | I | $PEt_3$ | 1 | 2 034, 1 993 | 0.521 | 119.60 |
| | I | $PPh_3$ | 5 | 2 017, 1 985 | 0.526 | 120.45 |
| (6) | Cl | ½dppe | 1 | 1 997 | | |
| | I | ½dppe | 1 | 1 969 | | |

[a] In $CH_2Cl_2$. [b] Ratio of the intensities of the i.r. absorptions due to the symmetric and asymmetric stretching vibrations of the carbonyl groups. [c] Angle between the carbonyl groups, calculated from $R_{sym}/R_{asym} = \cot^2\theta$.

The synthetic studies outlined above suggest a mechanism, illustrated in the Scheme, for the formation of (5) and (6) from (1) and (2), in which initial oxidation to give (3) or (4) followed by halogen-radical attack occurs. In support of this mechanism we note that formation of (5) from (1) only occurs if the added reagent is a strong enough oxidising agent to bring about the prior formation of (3) and (1). Thus there is no reaction between $I_2$ and [1; *n* = 1, L = $P(OPh)_3$] for which $E_P$ 0.88 V. The lack of reaction does not result from steric factors as [1; *n* = 0 or 5, L = $PPh_3$], for which the $E_P$ values are 0.59 and 0.37 V respectively, and $I_2$ readily yield [5; X = I, *n* = 0 or 5, L = $PPh_3$]. [The cone angle of $PPh_3$ (145 ± 2°) has been estimated [19] to be greater than that of $P(OPh)_3$ (121 ± 10°).] Similarly, whereas [N($C_6H_4$Br-*p*)$_3$][$SbCl_6$] reacts with [1; *n* = 1, L = $PMe_2Ph$ or $P(OPh)_3$] to give (5), no reaction occurs between [1; *n* = 1, L = $PMe_2Ph$ or $P(OPh)_3$] and [$NPr^n{}_4$][$SbCl_6$]. The hexachloroantimonate ion is an insufficiently strong oxidising agent * to bring about formation of (3) as a precursor to (5). Its reaction with (2; *n* = 1, L = ½dppe, $E_p$ −0.16 V), however, yields both (4) and (6). The necessity for halogen radicals in the formation of (6) from (4) is suggested by the observations that addition of $I_2$, or $I^-$, to a $CH_2Cl_2$ solution of [Mn($\eta$-$C_5H_4Me$)(CO)(dppe)][$BF_4$] {preformed by Ag[$BF_4$] oxidation of (2)} does not afford (6; X = I, *n* = 1, L = ½dppe), whereas direct addition of $I_2$ to (2; *n* = 1, L = ½dppe) in $CH_2Cl_2$ gives (6). [The reaction of $I_2$ with (2; *n* = 1, L = ½dppe) in hexane gives an immediate precipitate of (6).]



SCHEME Proposed mechanism for the formation of (5) and (6) from (1) and (2) respectively, illustrated by the reaction of [Mn($\eta$-$C_5H_5$)$(CO)_2$($PPh_3$)] with iodine

The addition of $SbCl_5$ to [M($\eta$-$C_6Me_6$)$(CO)_3$] (M = Cr, Mo, or W) gives [MCl($\eta$-$C_6Me_6$)$(CO)_3$][$SbCl_6$],[20] and similar reactions with [M($\eta$-$C_5H_5$)$(CO)_3$] (M = Mn [21] or Re [22]) have been observed. We now suggest that these

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* Preliminary measurements have shown that [$NPr^n{}_4$][$SbCl_6$] is reduced in an irreversible two-electron step at *ca.* 0.0 V [*versus* a calomel electrode (1 mol $dm^{-3}$ in LiCl)].

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reactions involve an initial one-electron-transfer step. When $SbCl_5$ was added to (1; $n = 1$, L = $PPh_3$) in $CH_2Cl_2$ the formation of (5; X = Cl, $n = 1$, L = $PPh_3$) was verified by i.r. spectroscopy. The reaction in hexane, however, yielded an unstable pink precipitate which exhibited, in $CH_2Cl_2$ solution, two carbonyl absorptions in the i.r. spectrum, coincident with those of (3; $n = 1$, L = $PPh_3$) generated from (1) by silver(I) ion oxidation. Finally, it is noteworthy that the oxidative addition of $Br_2$ to $[Re(\eta\text{-}C_5H_5)(CO)_3]$ to give [23] $[ReBr_2(\eta\text{-}C_5H_5)(CO)_2]$ no doubt occurs *via* the sequential formation $[Re(\eta\text{-}C_5H_5)(CO)_3]^+$ and $[ReBr(\eta\text{-}C_5H_5)(CO)_3]^+$ followed by reaction of the latter with bromide ion. Recent evidence for the intermediacy of an electron-transfer reaction in the oxidative addition of alkyl halides to *cis*-$[Mo(CO)_2(Me_2PCH_2CH_2PMe_2)_2]$ has been presented.[24]

*E.S.R.*—Cations (3) and (4) are paramagnetic and are expected to show e.s.r. signals. For the reasons presented above we were unable to record the spectra of (3). Those of (4; $n = 1$, L = $\frac{1}{2}$dppe, $PMePh_2$, or $PPh_3$), however, were studied over a range of temperature. Table 4 shows the values of $\langle g \rangle_{av.}$ and $\langle A_{Mn} \rangle_{av.}$ for the dppe complex generated in dichloroethane by the addition of different oxidising agents to (2; $n = 1$, L = $\frac{1}{2}$dppe). In general, only six broad lines due to coupling with the metal atom ($^{55}$Mn, $I = \frac{5}{2}$) were observed in the range 60 to −40 °C. No coupling to the phosphorus atoms ($^{31}$P, $I = \frac{1}{2}$) was observed although the broadness of the lines suggests such coupling to be present. The values of $\langle g \rangle_{av.}$ for each sample of (4; $n = 1$, L = $\frac{1}{2}$dppe) were equal to within experimental error, but those of $\langle A_{Mn} \rangle_{av.}$ differed significantly on changing the counter anion.

TABLE 4

E.s.r. data for $[Mn(\eta\text{-}C_5H_4Me)(CO)L_2]^+$ (4) [a]

| L | Oxidant | $\theta_c$/°C | $\langle g \rangle_{av.}$ | $\langle A_{Mn} \rangle_{av.}$ | $\langle A_P \rangle_{av.}$ |
|---|---|---|---|---|---|
| $\frac{1}{2}$dppe | $Ag[PF_6]$ [b] | 25 | 2.02 | 92.6 | |
| | $I_2$ [b] | 25 | 2.01 | 94.1 | |
| | $[N(C_6H_4Br\text{-}p)_3]$-$[SbCl_6]$ [b] | 25 | 2.01 | 74.1 | |
| | $[p\text{-}FC_6H_4N_2][BF_4]$ [b] | 60 to −40 | 2.01 | 93.8 | |
| $PPh_3$ | $[p\text{-}FC_6H_4N_2][BF_4]$ [c] | −60 | 2.02 | 93.2 | |
| | $[p\text{-}FC_6H_4N_2][BF_4]$ [c] | 0 | 2.02 | 93.2 | 24.5 |
| $PMePh_2$ | $[p\text{-}FC_6H_4N_2][BF_4]$ [c] | −60 to 0 | 2.02 | 93.2 | |
| | $[p\text{-}FC_6H_4N_2][BF_4]$ [c] | 20 | 2.02 | 93.2 | 24.5 |

[a] Generated *in situ* by addition of the oxidant to a solution of (2). The presence of cation (4) was verified by i.r. spectroscopy. [b] In dichloroethane. [c] In $CH_2Cl_2$.

Cations (4; $n = 1$, L = $PPh_3$ or $PMePh_2$), generated *in situ* by the oxidation of (2) by $[p\text{-}FC_6H_4N_2][BF_4]$ in $CH_2Cl_2$, showed temperature-dependent e.s.r. spectra. For example, for L = $PMePh_2$, the spectrum at −60 °C consisted of only six lines, with $\langle g \rangle_{av.}$ and $\langle A_{Mn} \rangle_{av.}$ equal to 2.02 and 93.2 G respectively, similar to those of (4; $n = 1$, L = $\frac{1}{2}$dppe). On warming the sample from −60 °C, hyperfine coupling on the centre lines of the sextet was observed; each of the lines began to resolve into a 1 : 2 : 1 triplet. At 10 °C resolution of the two centre lines was good while the outer two lines of the original sextet remained broad. The spectra observed between 0 and 10 °C allow $\langle A_{Mn} \rangle_{av.}$ and $\langle A_P \rangle_{av.}$ to be measured as 93.2 and 24.5 G respectively. Complete resolution of the e.s.r. spectrum of (4; $n = 1$, L = $PMePh_2$) into the 18 lines expected for hyperfine coupling to one manganese atom and two equivalent phosphorus atoms was not observed even on warming a sample of (4), generated in dichloroethane, to 60 °C. The variable-temperature spectrum of (4; $n = 1$, L = $PPh_3$) is similar to that of (4; $n = 1$, L = $PMePh_2$).

It is clear from the results presented above that, at low temperatures, nuclear quadrupole broadening of the e.s.r. spectra of (4) takes place and that such broadening is diminished at higher temperatures. The consistency of the value of $\langle g \rangle_{av.}$ with varying temperature shows that the spectral changes are due neither to the presence of more than one paramagnetic species in the sample nor to a change in spin state.

## EXPERIMENTAL

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. The complexes $[Mn(\eta\text{-}C_5H_{5-n}Me_n)(CO)_{3-x}L_x]$,[25] diazonium salts,[26] and $[N(C_6H_4Br\text{-}p)_3][SbCl_6]$ [27] were prepared by literature methods or by modifications thereof described below. U.v. irradiations were carried out using a 250-W mercury lamp (Hanovia, type 504/4). Nitrosonium and silver salts were purchased from Ozark Mahoning Co., Tulsa, Oklahoma. All the solvents were dried by standard methods and deoxygenated before use.

Infrared spectra were recorded on Perkin-Elmer PE 257 or PE 457 spectrophotometers using the × 10 expansion facility on the former, and were calibrated 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 solid sample of the diphenylpicrylhydrazyl (dpph) radical. Mass spectra were recorded on an A.E.I. MS902 instrument. Electrochemical studies were made using a Beckman Electroscan 30. Cyclic voltammetry was carried out using platinum-wire auxiliary and working electrodes and a calomel electrode (1 mol dm$^{-3}$ in LiCl) as reference. Solutions were 10$^{-3}$ mol dm$^{-3}$ in complex and 0.05 mol dm$^{-3}$ in $[NEt_4][ClO_4]$ as supporting electrolyte. Criteria for reversibility are based on the assumption that data for the complex under study should be similar to that found for the reversible one-electron oxidation of $[Ni\{S_2C_2(CN)_2\}_2]^{2-}$. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol. Melting points are uncorrected.

*Dicarbonyl(η-methylcyclopentadienyl)(triphenyl phosphite)-manganese*, $[Mn(\eta\text{-}C_5H_4Me)(CO)_2\{P(OPh)_3\}]$.—A solution of $[Mn(\eta\text{-}C_5H_4Me)(CO)_3]$ (1.1 g, 5 mmol) and $P(OPh)_3$ (2 g, 6.5 mmol) in toluene (50 cm$^3$) was irradiated (u.v. light) until

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all the tricarbonyl had reacted (140 h). The solvent was then removed and the residue was recrystallised from hot hexane to yield the product as pale yellow crystals, yield 1.83 g (73%). The *complexes* [Mn($\eta$-$C_5H_5$)$(CO)_2$L] [L = $PPh_3$ or $P(OPh)_3$] were made similarly; [Mn($\eta$-$C_5H_4$Me)-$(CO)_2$L] (L = $PPh_3$ or $PMe_2Ph$) and [Mn($\eta$-$C_5Me_5$)$(CO)_2$-$(PPh_3)$] were isolated from hot hexane after irradiation of the reactants in tetrahydrofuran (thf). All the complexes are yellow, air-stable, crystalline solids, which are moderately soluble in hexane and readily soluble in polar solvents such as $CH_2Cl_2$ to give yellow moderately air-stable solutions.

*Dicarbonyl(η-methylcyclopentadienyl)(triethylphosphine)-manganese*, [Mn($\eta$-$C_5H_4$Me)$(CO)_2$$(PEt_3)$].—Ultraviolet irradiation of [Mn($\eta$-$C_5H_4$Me)$(CO)_3$] (2.2 g, 10 mmol) and $PEt_3$ (1.2 g, 10 mmol) in thf (50 $cm^3$) for 150 h followed by removal of the solvent and chromatography of the oily residue on Florisil gave unchanged tricarbonyl, eluted with hexane, and a second yellow band, eluted with diethyl ether. Removal of solvent from the second fraction gave the product as a yellow oil, yield 1.0 g (33%). The *complexes* [Mn($\eta$-$C_5H_4$Me)$(CO)_2${$P(OMe)_3$}] and [Mn($\eta$-$C_5H_5$)-$(CO)_2$$(PEt_3)$] were prepared similarly. All the three complexes have properties similar to the other dicarbonyls described above.

*Carbonyl(η-methylcyclopentadienyl)bis(triphenylphosphine)-manganese*, [Mn($\eta$-$C_5H_4$Me)(CO)$(PPh_3)_2$].—Ultraviolet irradiation of a solution of [Mn($\eta$-$C_5H_4$Me)$(CO)_3$] (2.2 g, 10 mmol) and $PPh_3$ (8 g, 30 mmol) in thf (50 $cm^3$) for 70 h gave a dark red solution. Removal of the solvent and recrystallisation of the residue from hot hexane gave the product as red crystals, yield 6 g (87%). The *complexes* [Mn($\eta$-$C_5H_4$Me)(CO)$(PMePh_2)_2$] and [Mn($\eta$-$C_5H_5$)(CO)-$(PPh_3)_2$] were prepared similarly although the irradiation step for the latter was carried out in toluene. The complexes are red or orange solids which decompose slowly in air and light; decomposition can be retarded by storing them at 0 °C, under nitrogen, in the absence of light. They are slightly soluble in hexane but readily so in polar solvents such as $CH_2Cl_2$ to give fairly air-sensitive yellow solutions.

*[1,2-Bis(diphenylphosphino)ethane]carbonyl(η-methylcyclopentadienyl)manganese*, [Mn($\eta$-$C_5H_4$Me)(CO)(dppe)].—After irradiating (u.v. light) [Mn($\eta$-$C_5H_4$Me)$(CO)_3$] (3.3 g, 15 mmol) and $Ph_2PCH_2CH_2PPh_2$ (6 g, 15 mmol) in toluene (150 $cm^3$) until the required product was the predominant species present in the reaction mixture, the solvent was removed and the product was isolated by fractional crystallisation from hot ethanol, yield 4.35 g (52%). The complex is orange, stable in air, and soluble in polar solvents such as $CH_2Cl_2$ or acetone to give moderately air-stable orange solutions.

*[1,2-Bis(diphenylphosphino)ethane]carbonyl(η-methylcyclopentadienyl)manganese Hexafluorophosphate*, [Mn($\eta$-$C_5H_4$Me)(CO)(dppe)][$PF_6$].—To a stirred solution of [Mn($\eta$-$C_5H_4$Me)(CO)(dppe)] (0.3 g, 0.54 mmol) in $CH_2Cl_2$ (20 $cm^3$) was added solid [$PhN_2$][$PF_6$] (0.135 g, 0.54 mmol). After 2 min, hexane (25 $cm^3$) was added and on cooling the product was precipitated as orange crystals, yield 0.32 g (84%). The *salt* [Mn($\eta$-$C_5H_4$Me)(CO)(dppe)][$SbCl_6$] was prepared similarly, as orange plates, from [Mn($\eta$-$C_5H_4$Me)(CO)(dppe)] (0.41 g, 0.71 mmol) and [N($C_6H_4$Br-*p*)$_3$][$SbCl_6$] (0.29 g, 0.355 mmol) in $CH_2Cl_2$ (5 $cm^3$), yield 0.4 g (63%) (Found: C, 45.0; H, 3.7. Calc. for $C_{33}H_{31}Cl_6MnOP_2Sb$: C, 44.3; H, 3.5%).

The complexes are air-stable orange solids which dissolve in polar solvents such as acetone or $CH_2Cl_2$ to give orange moderately air-stable solutions.

*Dicarbonyl(dimethylphenylphosphine)iodo(η-methylcyclopentadienyl)manganese Nonaiodide*, [MnI($\eta$-$C_5H_4$Me)$(CO)_2$-$(PMe_2Ph)$][$I_9$].—To [Mn($\eta$-$C_5H_4$Me)$(CO)_2$$(PMe_2Ph)$] (0.06 g, 0.20 mmol) in acetone (10 $cm^3$) was added iodine (0.25 g, 1.00 mmol). After stirring for 5 min, diethyl ether (25 $cm^3$) was added to the deep red solution to precipitate the product as a dark red oil, yield 0.23 g (75%), $\Lambda$ ($10^{-4}$ mol $dm^{-3}$ in acetone) 150 S $cm^2$ $mol^{-1}$ (Found: C, 12.4; H, 1.6. Calc. for $C_{16}H_{18}I_{10}MnO_2P$: C, 12.5; H, 1.2%).

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