

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

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Cyclic-voltammetric studies in CH_2Cl_2 have shown that $[\text{Mn}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})_{3-x}\text{L}_x]$ [$n = 0, 1$, or 5 , $x = 1$, $\text{L} = \text{phosphine or phosphite}$ (1); $n = 0$ or 1 , $x = 2$, $\text{L} = \frac{1}{2}\text{dppe}$ ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), PPh_3 , or PMePh_2)] each undergo a reversible one-electron oxidation to $[\text{Mn}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})_{3-x}\text{L}_x]^+$ [$x = 1$ (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 $[\text{N}(\text{C}_6\text{H}_4\text{Br-}p)_3][\text{SbCl}_6]$, SbCl_5 , Br_2 , or I_2 , (1) and (2) afford the diamagnetic complexes $[\text{MnX}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})_{3-x}\text{L}_x]^+$ [$\text{X} = \text{Cl, Br, or I}$, $x = 1$ (5) or 2 (6)], *via* the attack of halogen radicals on (3) or (4). The relation between the oxidation potential, E_p , and $k(\text{CO})$, the force constant for the carbonyl-stretching vibrations, for (1), (2), and $[\text{Mn}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})_3]$ is discussed with reference to that previously reported for the isoelectronic chromium complexes $[\text{Cr}(\eta\text{-C}_6\text{Me}_6)(\text{CO})_2\text{L}]$.

We have previously shown² that the complexes $[\text{Cr}(\eta\text{-C}_6\text{Me}_6)(\text{CO})_2\text{L}]$ ($\text{L} = \text{phosphine or phosphite}$) undergo reversible one-electron oxidation reactions and that there is a linear relation between $\bar{\nu}(\text{CO})$ (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

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

isoelectronic with $[\text{Cr}(\eta\text{-C}_6\text{Me}_6)(\text{CO})_2\text{L}]$. Preliminary studies² revealed a good agreement between the measured values of E_p for $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{L}]$ [$\text{L} = \text{P(OPh)}_3$, PPh_3 , or PEt_3] and those calculated using the relation between E_p and $\bar{\nu}(\text{CO})$ (av.) for $[\text{Cr}(\eta\text{-C}_6\text{Me}_6)(\text{CO})_2\text{L}]$. We have now found, however, by investigating a large number of tricarbonyl(η -cyclopentadienyl)-manganese derivatives $[\text{Mn}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})_{3-x}\text{L}_x]$ [$x = 1$ (1) or 2 (2)], that there is a direct relation between

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 $[\text{Mn}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})_3\text{L}_x]^+$ [$x = 1$ (3) or 2 (4)], preliminary

prepared by modifications of published methods (see Experimental section) and were characterised fully before use (Table 1). Cyclic-voltammetric studies in CH_2Cl_2 showed that each complex underwent only one redox process (in the range ± 1.5 V) at the stationary

TABLE 1
Analytical and m.p. data for $[\text{Mn}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})_2\text{L}]$ (1) and $[\text{Mn}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})\text{L}_2]$ (2)

Complex	L	n	Colour	M.p. ($^\circ\text{C}$)	Yield (%)	M ^a	Analysis (%) ^b	
							C	H
(1)	P(OPh) ₃	0	Yellow	116—118	45	486	61.5 (61.7)	4.4 (4.2)
	PPh ₃	0	Yellow	162—164	52	438	68.3 (68.5)	4.6 (4.6)
	PEt ₃	0	Yellow oil		43	294	53.3 (53.1)	7.0 (6.9)
	P(OPh) ₃	1	Yellow	78—80	73	500	62.9 (62.7)	4.6 (4.5)
	P(OMe) ₃	1	Yellow oil		32	314	42.7 (42.1)	5.5 (5.1)
	PPh ₃	1	Yellow	119—120	44	452	68.6 (69.0)	4.8 (4.9)
	PMe ₂ Ph	1	Yellow	60—63	27	328	58.5 (58.5)	5.7 (5.5)
	PEt ₃	1	Yellow oil		33	308	55.2 (54.6)	7.6 (7.2)
	PPh ₃	5	Yellow	Decomp. > 165	48	508	71.0 (70.9)	6.0 (6.0)
	PPh ₃	0	Red	Decomp. > 149	24		74.5 (75.0)	5.3 (5.3)
(2)	PPh ₃	1	Red	Decomp. > 133	87		75.4 (75.2)	5.6 (5.3)
	PMePh ₂	1	Orange	Decomp. > 130	61		70.2 (70.5)	6.0 (5.9)
	$\frac{1}{2}$ dppe	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 $[\text{Mn}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})_2\text{L}]^z$ [$z = 0$ (1) or 1 (3)] and $[\text{Mn}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})\text{L}_2]^z$ [$z = 0$ (2) or 1 (4)]

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

^a For the reversible one-electron oxidation of $[\text{Ni}\{\text{S}_2\text{C}_2(\text{CN})_2\}_2]^{2-}$: $(E_p)_{\text{ox}} - (E_p)_{\text{red}} = 140$ mV; $(i_p)_{\text{ox}} = 3.0$ μA ; $(i_p)_{\text{red}} = 2.9$ μA .
^b In 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 CH_2Cl_2 by addition of $\text{Ag}[\text{BF}_4]$. ^f Generated in CH_2Cl_2 by addition of $[\text{PhN}_2][\text{PF}_6]$.

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 $[\text{MnX}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})_3\text{L}_x]^+$ [$X = \text{Cl}, \text{Br}, \text{or I}$, $x = 1$ (5) or 2 (6)] from (1) or (2) and $[\text{N}(\text{C}_6\text{H}_4\text{Br-}p)_3][\text{SbCl}_6]$, SbCl_5 , Br_2 , or I_2 .

RESULTS AND DISCUSSION

Electrochemical Studies.—Complexes (1) and (2) were

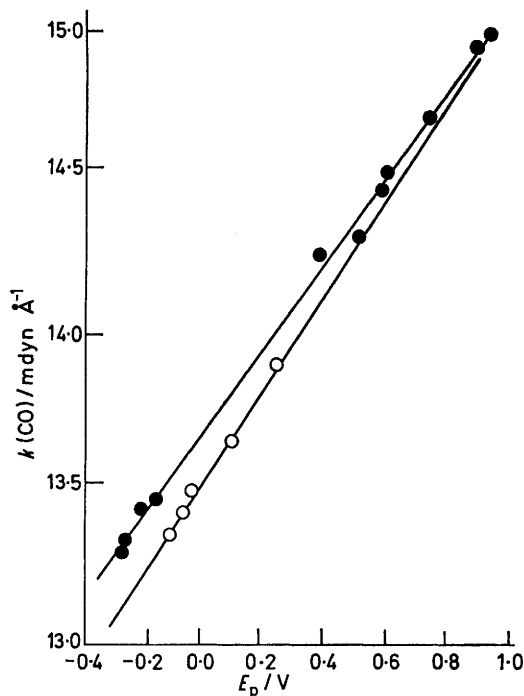
³ P. M. Treichel, K. P. Wagner, and H. J. Mueh, *J. Organometallic Chem.*, 1975, **86**, C13.

platinum-wire electrode; unlike other workers,^{4,5} we did not detect more than one oxidation step. A comparison of the values of $(E_p)_{\text{ox}} - (E_p)_{\text{red}}$, $(i_p)_{\text{ox}}$, and $(i_p)_{\text{red}}$ (Table 2) for (1) and (2) with those for the electron-transfer process $[\text{Ni}\{\text{S}_2\text{C}_2(\text{CN})_2\}_2]^{2-} \rightleftharpoons [\text{Ni}\{\text{S}_2\text{C}_2(\text{CN})_2\}_2]^-$ confirmed that in all the cases (1) and (2) are oxidised in a reversible one-electron step, to $[\text{Mn}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)-$

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 = PPh₃) by PPh₃ to give (2; *n* = 0, L = PPh₃) resulted in a shift of *E*_p to more negative potentials by



Plot of *k*(CO) against *E*_p for [Mn(η-C₅H_{5-n}Me_n)(CO)_{3-x}L_x] (●) and [Cr(η-C₆Me₆)(CO)₂L] (○) ² in CH₂Cl₂

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.

A plot of $\bar{\nu}(\text{CO})$ (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(η-C₆Me₆)(CO)₂L]. The

* 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.

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(η-C₅H₅)(CO)₂(PPh₃)]⁷ and [Cr(η-C₆Me₆)(CO)₂(PPh₃)]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(η-C₆Me₆)(CO)₃] and [Mn(η-C₅H_{5-n}Me_n)(CO)₃] (*n* = 0, 1, or 5). Although poor agreement between the data for [Cr(η-C₆Me₆)(CO)₃] and for [Cr(η-C₆Me₆)(CO)₂L] (L = phosphine or phosphite) was found when using $\bar{\nu}(\text{CO})$ (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(η-C₅H_{5-n}Me_n)(CO)₂L] (1) and for [Mn(η-C₅H_{5-n}Me_n)(CO)L₂] (2). It seems reasonable to assume, therefore, that the plot is also valid for the parent tricarbonyls. The *E*_p values of [Mn(η-C₅H_{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(η-C₅H_{5-n}Me_n)(CO)₃] (*n* = 0 and 1) may be made from the oxidation potentials measured for [Mn(η-C₅H_{5-n}Me_n)(CO)_{3-x}(PPh₃)_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(η-C₅H_{5-n}Me_n)(CO)₃] in CH₂Cl₂, the reversible oxidation of the cyclopentadienyl complex (*n* = 0) has been observed³ in CF₃CO₂H [*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 CH₂Cl₂, (1) reacted with [NO][PF₆] to give a

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 known¹² nitrosyl complexes $[\text{Mn}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})_2(\text{NO})]^+$ and $[\text{Mn}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})(\text{NO})\text{L}]^+$ by displacement of L or CO. For (1; L = PPh_3 , $n = 5$) preferential displacement of L occurred to give $[\text{Mn}(\eta\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{NO})]^+$ 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), $[\text{NO}][\text{PF}_6]$ in CH_2Cl_2 afforded mixtures of the nitrosyl complexes $[\text{Mn}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})(\text{NO})\text{L}]^+$ and the paramagnetic cations (4). The observation of both oxidation and substitution of (2) contrasts with the behaviour of $[\text{Cr}(\eta\text{-C}_6\text{Me}_6)(\text{CO})_2\text{L}]$ for which only substitution occurs.²

No identifiable products resulted from the reaction of (1) with $[\text{PhN}_2][\text{PF}_6]$, either in CH_2Cl_2 or in acetone. With (2; L = $\frac{1}{2}\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe), $n = 1$), however, ready oxidation occurred to give (4) exclusively and addition of hexane to the reaction mixture gave orange crystals of $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})(\text{dppe})][\text{PF}_6]$. 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 = $\frac{1}{2}\text{dppe}$, $n = 1$)], and by i.r. spectroscopy (Table 2) which showed an increase in $\bar{\nu}(\text{CO})$ 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 $[\text{PhN}_2][\text{PF}_6]$ in CH_2Cl_2 but the resulting cations were not isolated as stable solids. They, and (4; L = $\frac{1}{2}\text{dppe}$, $n = 1$) were, however, characterised by their solution e.s.r. spectra (see below).

Our previous studies² with $[\text{Cr}(\eta\text{-C}_6\text{Me}_6)(\text{CO})_2\text{L}]$ allowed us to estimate $E(\text{NO}^+)$ and $E(\text{PhN}_2^+)$, 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 $-0.16 < E_{\text{Mn}}(\text{PhN}_2^+) < 0.37$ V. This does not allow us to say whether there is a dependence of $E(\text{PhN}_2^+)$ on the metal atom. That both substitution and oxidation of (2) with NO^+ occurs suggests that $E_{\text{Mn}}(\text{NO}^+)$ is in the region of -0.16 to -0.28 V, in agreement with the finding² of $-0.22 < E_{\text{Cr}}(\text{NO}^+) < -0.11$ V.

Although neither $[\text{NO}]^+$ nor $[\text{PhN}_2]^+$ oxidised the dicarbonyls (1) to (3), the addition of $\text{Ag}[\text{BF}_4]$ 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 $[\text{Mn}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]^+$ from $[\text{Mn}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]$ by controlled-potential electrolysis.⁵

¹² T. A. James and J. A. McCleverty, *J. Chem. Soc. (A)*, 1970, 850; H. Br  nner, *Z. anorg. Chem.*, 1969, **368**, 120; R. B. King and A. Efraty, *Inorg. Chem.*, 1969, **8**, 2374.

¹³ R. B. King, A. Efraty, and W. M. Douglas, *J. Organometallic Chem.*, 1973, **56**, 345.

The i.r. spectra (Table 2) of the reaction mixtures each showed two bands in the carbonyl-stretching region, shifted to higher wavenumbers by $100\text{--}120\text{ cm}^{-1}$ from the values for (1), as expected for the formation of (3). Similar changes in the i.r. spectra of $[\text{Cr}(\eta\text{-C}_6\text{Me}_6)(\text{CO})_2\text{L}]$ have been found² on oxidation to the monocations $[\text{Cr}(\eta\text{-C}_6\text{Me}_6)(\text{CO})_2\text{L}]^+$. 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 $\text{Ag}[\text{PF}_6]$ to (2; $n = 1$, L = $\frac{1}{2}\text{dppe}$, 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 $[\text{PhN}_2][\text{PF}_6]$.

Triarylammonio-salts have been used in the oxidation of organic substrates¹⁴ and have found limited use as oxidants in organometallic chemistry.¹⁵ The reaction of $[\text{N}(\text{C}_6\text{H}_4\text{Br-}p)_3][\text{SbCl}_6]$ with (2; $n = 1$, L = $\frac{1}{2}\text{dppe}$) 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 micro-analytical 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 $[\text{N}(\text{C}_6\text{H}_4\text{Br-}p)_3]^+$ and the anion $[\text{SbCl}_6]^-$ can function as oxidising agents and studies¹⁶ with the latter ion have shown that the products formed may include $[\text{SbCl}_4]^-$, $[\text{Sb}_2\text{Cl}_9]^{3-}$, or $[\text{SbCl}_6]^{3-}$ as the counter anion. We feel, therefore, that the counter anion present in the product of the oxidation of (2; $n = 1$, L = $\frac{1}{2}\text{dppe}$) by $[\text{N}(\text{C}_6\text{H}_4\text{Br-}p)_3][\text{SbCl}_6]$ may not be $[\text{SbCl}_6]^-$. The addition of greater quantities of $[\text{N}(\text{C}_6\text{H}_4\text{Br-}p)_3][\text{SbCl}_6]$ 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 $[\text{MnCl}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})(\text{dppe})]^+$ on the basis of the following results. The reaction of $[\text{N}(\text{C}_6\text{H}_4\text{Br-}p)_3][\text{SbCl}_6]$ 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 $[\text{MnX}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})_2\text{L}]^+$ (5) or $[\text{MnX}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})\text{L}_2]^+$ (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

¹⁴ C. E. H. Bawn, F. A. Bell, and A. Ledwith, *Chem. Comm.*, 1968, 599.

¹⁵ W. E. Williams and F. J. Lalor, *J.C.S. Dalton*, 1973, 1329.

¹⁶ G. W. Cowell, A. Ledwith, A. C. White, and H. J. Woods, *J. Chem. Soc. (B)*, 1970, 227.

in *vacuo* and analysed (C and H only) for $[\text{MnI}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2(\text{PMe}_2\text{Ph})][\text{I}_3]$. Based on this formula, the measured conductivity (Λ 150 S cm² 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

TABLE 3

I.r. data ^a for $[\text{MnX}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})_2\text{L}]^+$ (5) and $[\text{MnX}(\eta\text{-C}_5\text{H}_{5-n}\text{Me}_n)(\text{CO})\text{L}_2]^+$ (6)

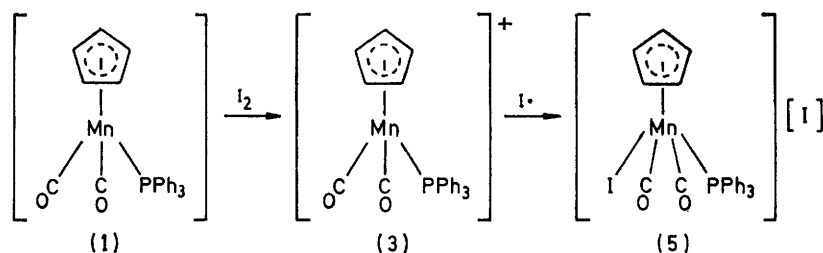
Complex	X	L	n	$\bar{\nu}(\text{CO})/\text{cm}^{-1}$	$R_{\text{sym}}/R_{\text{asym}}$ ^b	2θ ^c /°
(5)	I	PPh ₃	0	2 045, 2 008	0.213	133.72
	Cl	P(OPh) ₃	1	2 082, 2 033	1.068	58.95
	Br	P(OPh) ₃	1	2 069, 2 033	0.887	105.35
	Cl	PPh ₃	1	2 067, 2 029	0.967	102.65
	Br	PPh ₃	1	2 057, 2 018	0.465	122.17
	I	PPh ₃	1	2 038, 2 000	0.335	128.20
	Cl	PMe ₂ Ph	1	2 064, 2 005	0.840	106.93
	Br	PMe ₂ Ph	1	2 052, 2 012	0.430	123.50
	I	PMe ₂ Ph	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	$\frac{1}{2}$ dppe	1	1 997		
	I	$\frac{1}{2}$ dppe	1	1 969		

^a In CH₂Cl₂. ^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 $R_{\text{sym}}/R_{\text{asym}} = \cot^2\theta$.

clear that varying any one of X, L, or *n* results in a shift of $\bar{\nu}(\text{CO})$, confirming the presence of the halogen, 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 $[\text{MnCl}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\{\text{P(OPh)}_3\}]^+$ is somewhat surprising.

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 I₂ 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 = PPh₃], for which the *E*_P values are 0.59 and 0.37 V respectively, and I₂ readily yield [5; X = I, *n* = 0 or 5, L = PPh₃]. [The cone angle of PPh₃ (145 ± 2°) has been estimated¹⁹ to be greater than that of P(OPh)₃ (121 ± 10°).] Similarly, whereas $[\text{N}(\text{C}_6\text{H}_4\text{Br-}p)_3][\text{SbCl}_6]$ reacts with [1; *n* = 1, L = PMe₂Ph or P(OPh)₃] to give (5), no reaction occurs between [1; *n* = 1, L = PMe₂Ph or P(OPh)₃] and $[\text{NPr}^n_4][\text{SbCl}_6]$. 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 = $\frac{1}{2}$ dppe, *E*_P -0.16 V), however, yields both (4) and (6). The necessity for halogen radicals in



SCHEME Proposed mechanism for the formation of (5) and (6) from (1) and (2) respectively, illustrated by the reaction of $[\text{Mn}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{PPh}_3)]$ with iodine

cyclopentadienyl ring, and the ligand L. In addition a comparison of the values of $\bar{\nu}(\text{CO})$ for (5) with those of the isoelectronic neutral complexes $[\text{MoX}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{L}]$ ¹⁷ shows the expected shift to higher frequency for cations (5). It is interesting to note that both *cis* and *trans* isomers of $[\text{MoX}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{L}]$ 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 relation¹⁸ $R_{\text{sym}}/R_{\text{asym}} = \cot^2\theta$, where *R*_{sym} and *R*_{asym} refer to the

the formation of (6) from (4) is suggested by the observations that addition of I₂, or I⁻, to a CH₂Cl₂ solution of $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})(\text{dppe})][\text{BF}_4]$ {preformed by Ag[BF₄] oxidation of (2)} does not afford (6; X = I, *n* = 1, L = $\frac{1}{2}$ dppe), whereas direct addition of I₂ to (2; *n* = 1, L = $\frac{1}{2}$ dppe) in CH₂Cl₂ gives (6). [The reaction of I₂ with (2; *n* = 1, L = $\frac{1}{2}$ dppe) in hexane gives an immediate precipitate of (6).]

The addition of SbCl₅ to $[\text{M}(\eta\text{-C}_6\text{Me}_6)(\text{CO})_3]$ (M = Cr, Mo, or W) gives $[\text{MCl}(\eta\text{-C}_6\text{Me}_6)(\text{CO})_3][\text{SbCl}_6]$,²⁰ and similar reactions with $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]$ (M = Mn²¹ or Re²²) have been observed. We now suggest that these

* Preliminary measurements have shown that $[\text{NPr}^n_4][\text{SbCl}_6]$ is reduced in an irreversible two-electron step at ca. 0.0 V [versus a calomel electrode (1 mol dm⁻³ in LiCl)].

¹⁷ J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, 1970, **92**, 5852.

¹⁸ D. Steele, *Quart. Rev.*, 1964, **18**, 21.

¹⁹ C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

²⁰ M. H. B. Stiddard and R. E. Townsend, *J. Chem. Soc. (A)*, 1969, 2355.

²¹ W. E. McEwen, J. A. Manning, and J. Kleinberg, *Tetrahedron Letters*, 1964, 2195.

²² R. B. King, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2119.

reactions involve an initial one-electron-transfer step. When SbCl_5 was added to (1; $n = 1$, $L = \text{PPh}_3$) in CH_2Cl_2 the formation of (5; $X = \text{Cl}$, $n = 1$, $L = \text{PPh}_3$) 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; $n = 1$, $L = \text{PPh}_3$) generated from (1) by silver(I) ion oxidation. Finally, it is noteworthy that the oxidative addition of Br_2 to $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]$ to give $^{23}[\text{ReBr}_2(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]$ no doubt occurs *via* the sequential formation $[\text{Re}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]^+$ and $[\text{ReBr}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]^+$ 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 $\text{cis}[\text{Mo}(\text{CO})_2(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2]$ 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; $n = 1$, $L = \frac{1}{2}\text{dppe}$, PMePh_2 , or PPh_3), however, were studied over a range of temperature. Table 4 shows the values of $\langle g \rangle_{\text{av.}}$ and

TABLE 4

E.s.r. data for $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})\text{L}_2]^+$ (4) ^a

L	Oxidant	$\theta_c/^\circ\text{C}$	$\langle g \rangle_{\text{av.}}$	$\langle A_{\text{Mn}} \rangle_{\text{av.}}$	$\langle A_{\text{P}} \rangle_{\text{av.}}$
$\frac{1}{2}\text{dppe}$	$\text{Ag}[\text{PF}_6]$ ^b	25	2.02	92.6	
	I_2	25	2.01	94.1	
	$[\text{N}(\text{C}_6\text{H}_4\text{Br}-p)_3]^-$	25	2.01	74.1	
	$[\text{SbCl}_6]$ ^b				
PPh_3	$[p\text{-FC}_6\text{H}_4\text{N}_2][\text{BF}_4]$ ^c	60 to -40	2.01	93.8	
	$[p\text{-FC}_6\text{H}_4\text{N}_2][\text{BF}_4]$ ^c	-60	2.02	93.2	
	$[p\text{-FC}_6\text{H}_4\text{N}_2][\text{BF}_4]$ ^c	0	2.02	93.2	24.5
PMePh_2	$[p\text{-FC}_6\text{H}_4\text{N}_2][\text{BF}_4]$ ^c	-60 to 0	2.02	93.2	
	$[p\text{-FC}_6\text{H}_4\text{N}_2][\text{BF}_4]$ ^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 .

$\langle A_{\text{Mn}} \rangle_{\text{av.}}$ for the dppe complex generated in dichloroethane by the addition of different oxidising agents to (2; $n = 1$, $L = \frac{1}{2}\text{dppe}$). 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 $\langle g \rangle_{\text{av.}}$ for each sample of (4; $n = 1$, $L = \frac{1}{2}\text{dppe}$) were equal to within experimental error, but those of $\langle A_{\text{Mn}} \rangle_{\text{av.}}$ differed significantly on changing the counter anion.

Cations (4; $n = 1$, $L = \text{PPh}_3$ or PMePh_2), generated *in situ* by the oxidation of (2) by $[p\text{-FC}_6\text{H}_4\text{N}_2][\text{BF}_4]$ in CH_2Cl_2 , showed temperature-dependent e.s.r. spectra. For example, for $L = \text{PMePh}_2$, the spectrum at -60°C consisted of only six lines, with $\langle g \rangle_{\text{av.}}$ and $\langle A_{\text{Mn}} \rangle_{\text{av.}}$ equal to 2.02 and 93.2 G respectively, similar to those of (4; $n = 1$, $L = \frac{1}{2}\text{dppe}$). 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 $\langle A_{\text{Mn}} \rangle_{\text{av.}}$ and $\langle A_{\text{P}} \rangle_{\text{av.}}$ to be measured as 93.2 and 24.5 G respectively. Complete resolution of the e.s.r. spectrum of (4; $n = 1$, $L = \text{PMePh}_2$) 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; $n = 1$, $L = \text{PPh}_3$) is similar to that of (4; $n = 1$, $L = \text{PMePh}_2$).

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 $\langle g \rangle_{\text{av.}}$ 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 $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})_n(\text{CO})_{3-n}\text{L}_n]$,²⁵ diazonium salts,²⁶ and $[\text{N}(\text{C}_6\text{H}_4\text{Br}-p)_3][\text{SbCl}_6]$ 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 $\times 10$ expansion facility on the former, and were calibrated against the absorption band of polystyrene at 1601 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 $10^{-3}\text{ mol dm}^{-3}$ in complex and 0.05 mol dm^{-3} in $[\text{NET}_4][\text{ClO}_4]$ 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 $[\text{Ni}\{\text{S}_2\text{C}_2(\text{CN})_2\}_2]^{2-}$. 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, $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\{\text{P}(\text{OPh})_3\}]$.—A solution of $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_3]$ (1.1 g, 5 mmol) and $\text{P}(\text{OPh})_3$ (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 $[\text{Mn}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{L}]$ [$\text{L} = \text{PPh}_3$ or P(OPh)_3] were made similarly; $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{L}]$ ($\text{L} = \text{PPh}_3$ or PMe_2Ph) and $[\text{Mn}(\eta\text{-C}_5\text{Me}_5)(\text{CO})_2(\text{PPh}_3)]$ 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, $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2(\text{PEt}_3)]$.—Ultraviolet irradiation of $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_3]$ (2.2 g, 10 mmol) and PEt_3 (1.2 g, 10 mmol) in thf (50 cm³) 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 $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\{\text{P(OMe)}_3\}]$ and $[\text{Mn}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{PEt}_3)]$ were prepared similarly. All the three complexes have properties similar to the other dicarbonyls described above.

Carbonyl(η -methylcyclopentadienyl)bis(triphenylphosphine)-manganese, $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})(\text{PPh}_3)_2]$.—Ultraviolet irradiation of a solution of $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_3]$ (2.2 g, 10 mmol) and PPh_3 (8 g, 30 mmol) in thf (50 cm³) 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 $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})(\text{PMePh}_2)_2]$ and $[\text{Mn}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)_2]$ 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, $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})(\text{dppe})]$.—After irradiating (u.v. light) $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_3]$ (3.3 g, 15 mmol) and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (6 g, 15 mmol) in toluene (150 cm³) 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, $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})(\text{dppe})][\text{PF}_6]$.—To a stirred solution of $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})(\text{dppe})]$ (0.3 g, 0.54 mmol) in CH_2Cl_2 (20 cm³) was added solid $[\text{PhN}_2][\text{PF}_6]$ (0.135 g, 0.54 mmol). After 2 min, hexane (25 cm³) was added and on cooling the product was precipitated as orange crystals, yield 0.32 g (84%). The salt $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})(\text{dppe})][\text{SbCl}_6]$ was prepared similarly, as orange plates, from $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})(\text{dppe})]$ (0.41 g, 0.71 mmol) and $[\text{N}(\text{C}_6\text{H}_4\text{Br-}p)_3][\text{SbCl}_6]$ (0.29 g, 0.355 mmol) in CH_2Cl_2 (5 cm³), yield 0.4 g (63%) (Found: C, 45.0; H, 3.7. Calc. for $\text{C}_{33}\text{H}_{31}\text{Cl}_6\text{MnOP}_2\text{Sb}$: 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, $[\text{MnI}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2(\text{PMe}_2\text{Ph})][\text{I}_9]$.—To $[\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2(\text{PMe}_2\text{Ph})]$ (0.06 g, 0.20 mmol) in acetone (10 cm³) was added iodine (0.25 g, 1.00 mmol). After stirring for 5 min, diethyl ether (25 cm³) was added to the deep red solution to precipitate the product as a dark red oil, yield 0.23 g (75%), Λ (10^{-4} mol dm⁻³ in acetone) 150 S cm² mol⁻¹ (Found: C, 12.4; H, 1.6. Calc. for $\text{C}_{16}\text{H}_{18}\text{I}_{10}\text{MnO}_2\text{P}$: C, 12.5; H, 1.2%).

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