Contribution from the Department of Chemistry,
University of Essex, Colchester, Essex, United Kingdom

The Reaction between Manganese Carbonyl and Triphenylphosphine

J. R. Miller* and D. H. Myers

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The reaction of manganese carbonyl and triphenyl phosphine has been investigated under a variety of conditions. Binuclear and mononuclear products were obtained. By carrying out the reaction in an e.s.r. cavity it has been verified that paramagnetic products are formed during the reaction, but it has not been possible to isolate them. The mononuclear product isolated was diamagnetic and is believed to be the trans *isomer of* $HMn(CO)_4PPh_3$.

Introduction

The reaction of manganese carbonyl and triphenylphosphine has been much investigated since Hieber and Freyer[1] reported that heating these substances in xylene yielded a paramagnetic solid of molecular weight 420 which was claimed to have the formula $Ph_3PMn(CO)_4$.

Osborne and Stiddard[2] used ultraviolet radiation to initiate the reaction and found that it produced the dimeric, diamagnetic species $[Ph_3PMn(CO)_4]_2$. These authors further claimed that they could obtain only the dimer from the reaction carried out using Hieber and Freyer's conditions.

Ugo and Bonati[3] used the more vigorous conditions of refluxing a 5:1 excess of triphenylphosphine in xylene for 80 hours under nitrogen, and found that two carbonyl groups per manganese atom were substituted and the metal-metal bond was broken.

The product was diamagnetic and the presence of a high-field signal in the proton magnetic resonance spectra confirmed the nature of this product as $HMn(CO)_3(PPh_3)_2$.

Manning[4] repeated the work of Hieber *et al.* and Osborne *et al.*, and isolated identical products from both preparations. These products however had molecular weights of 670, magnetic moments in the range 1.10-1.70 B.M. and infrared spectra consistent with either mononuclear carbonyls of approximately C_{4v} symmetry or binuclear carbonyls of approximately D_{4d} symmetry.

Wawersik and Basolo[5] agreed with Osborne and Stiddard in being unable to isolate the mononuclear species and suggested that the paramagnetism observed by other workers was due to impurities produced by thermal decomposition, during the reaction, of the dimeric $[Ph_3PMn(CO)_4]_2$.

Recently Wojcicki and Hartman[6] isolated a compound whose analysis and molecular weight agreed with the formulation $Ph_3PMn(CO)_4$ but which was diamagnetic. The authors suggested the material might be *trans*–$H(PPh_3)Mn(CO)_4$. The material was obtained by reaction of $PhCH_2SO_2 . Mn(CO)_5$ with triphenylphosphine.

In this Paper we report attempts to isolate and characterise the mononuclear derivative reported as a product from the direct reaction of manganese carbonyl and triphenylphosphine, and to investigate further the occurrence of paramagnetic species.

Experimental Section

The following reactions were carried out in an atmosphere of dry, deoxygenated nitrogen. Solvents were dried, distilled and stored under nitrogen prior to use.

(a) Manganese carbonyl and triphenylphosphine, in a 1:3 mole ratio, were dissolved in cyclohexane and the mixture irradiated for 12 hours at room temperature in a sealed, evacuated Carius tube by a Mazda mercury arc lamp.

(b) Experiment (a) was repeated using *p*-xylene as solvent. Instead of irradiating, the mixture was heated at 120°C in an oil-bath for 16 hours.

(c) Manganese carbonyl and triphenylphosphine in a 1:2 mole ratio were finely powdered, mixed, and heated at 120-140°C for 4 hours under vacuum (0.5 mm Hg).

(d) Experiment (c) was repeated with the heating continued for 18 hours.

(e) Equimolar proportions of $C_6H_2CH_2SO_5Mn(CO)_5$ (prepared as in the literature[6]) and triphenylphosphine were intimately mixed, heated at 90°C for 3 hours and then at 65°C for 14 hours. The resulting red solid was extracted with benzene.

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(1) W. Hieber and W. Freyer, *Chem. Ber.*, *92*, 1765 (1959)
(2) A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 634 (1964).
(3) R. Ugo and F. Bonati, *J. Organometallic Chem.*, *8*, 189 (1967).
(4) A R. Manning, Ph. D. Thesis, Manchester Univesity, 1966.
(5) H. Wawersik and F. Basolo, *Chem. Comm.*, 366 (1966).

(6) A. Wojcicki and F. Hartman, *J. Amer. Chem. Soc.*, *88*, 844 (1966).

The solid products from these reactions were isolated from any solvent by pumping and were then recrystallised from benzene. Further purifications were carried out by chromatography using a 25×3 cm. Florisil (60/80) column, which was eluted with benzene.

DiarsMn(CO)$_3$, *cis*–HMn(CO)$_4$PPh$_3$ and *cis*–HMn(CO)$_4$PBu$_3$ were prepared as in the literature.[7,8]

Micro-analyses and osmometric molecular weights in benzene were carried out by A. Bernhardt and by the micro-analysis laboratory at Manchester University. The results are presented in Table I.

Table I. Analyses and Molecular Weights for Products (a) - (e).

Expt.	Found %C	%H	M.Wt.
(a)	61.3	3.5	837
(b)	61.3	3.6	435
(c)	62.0	3.6	475
(d)	62.5	3.5	500
(e)	62.0	3.3	—
Calc. for $C_{22}H_{15}MnO_4P$	61.5	3.5	429 (or 858 if dimeric)

Products from reaction (a) will be termed D and those from (b)-(e), which were indistinguishable, will be termed M. In one case, a sample from experiment (c) appeared to be of type M before chromatography, and of type D after chromatography. Otherwise the molecular weights were not changed by chromatography.

Magnetic susceptibility measurements on solids were made by the Gouy method in a nitrogen atmosphere. A permanent magnet was used for room-temperature measurements and an apparatus similar to that of Figgis and Nyholm[9] for measurements down to 90°K.

Magnetic susceptibilities in solution were measured using a Varian A60 n.m.r. spectrometer. The solution was placed in a normal n.m.r. tube, in which was placed a capillary tube containing pure solvent; the capillary was centralised by the vortex formed on spinning. Using xylene as solvent, splitting of the sharp methyl peaks gives a measure of the susceptibility of the solution.[10]

Electron spin resonance spectra were obtained on a 12 inch Varian V4502 spectrometer, employing a V 4540 temperature controller and 100 KHz modulation. Hyperfine splitting was observed at 90°K.

Infrared spectra were measured on Perkin-Elmer 221 and 257 instruments, and carbon disulphide solvent.

Mass spectra were measured on A.E.I. MS9 and MS12 instruments, using a 70 ev. beam. In all cases particular care was taken to minimise exposure of the samples to air.

Results

Magnetic Measurements. Room-temperature magnetic moments are shown in Table II. The molecular weights are those determined for the same sample, although theoretical values were used in the calculation of molar susceptibility. Samples from preparations (c), (d), and (e) gave data very similar to those from (b), with one exception from preparation (c) which has been mentioned. Interpretation of these data needs care because of uncertainty in the diamagnetic correction, the possible appearance of temperature-independent paramagnetism (TIP), and the possibility of antiferromagnetic species being present.

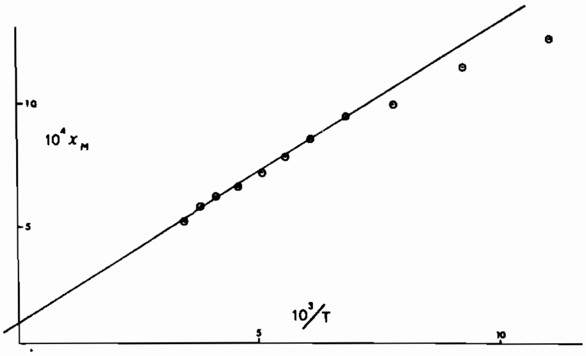

Figure 1. Magnetic Susceptibility of M (unchromatographed) *vs.* 1/T. The straight line is the least-squares line through the high-temperature points.

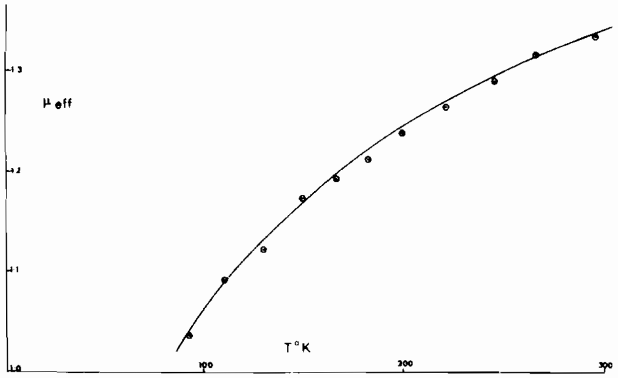

Figure 2. The Magnetic Moment of M (unchromatographed) *vs.* T.

Variable temperature measurements were made on the mononuclear samples and on the binuclear sample before chromatography. It was assumed that the data in Table II verified that the chromatographed D samples are diamagnetic. The unchromatographed sample of M showed smooth changes of magnetic moment with temperature. The data are shown in Table III and plotted in Figures 1 and 2. The molar suscepti-

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(7) R. S. Nyholm and D. V. R. Rao, *Proc. Chem. Soc.*, 130 (1959).
(8) W. Hieber, G. Faulhaber, and F. Theubert, *Z. Anorg. Chem.*, *314*, 125 (1963).
(9) B. N. Figgs and R. S. Nyholm, *J. Chem. Soc.*, 331 (1959).
(10) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

Table II. Room-Temperature Magnetic Data for Reactions Products.

Sample	$10^6\chi_g$	$10^6\chi_m$	$10^6\chi_m^{corr.}$	T°K	μ_{eff}B.M.	M.Wt.
(a) recryst.	-0.05	-41	431	292.7	0.98	850
(a) chromatographed	-0.51	-434	38	291.2	0.30	835
(b) recryst.	1.24	535	771	290.7	1.37	480
(b) chromatographed	-0.20	-86	150	291.0	0.60	400

Theoretical molecular weights of 858 and 429 were used for samples (a) and (b) respectively in the calculation of χ_m. All units are c.g.s.

Table III. The Variation of χ_m and μ_{effi} with Temperature for M Before Chromatography.

$10^6\chi_m$	510	570	608	665	711	771	844	933	991	1147	1257
T°K	296.5	267.0	245.3	221.5	199.0	181.9	165.7	148.2	129.1	108.5	90.8
μ_{eff}	1.33	1.31	1.29	1.26	1.26	1.21	1.20	1.18	1.13	1.10	1.04

A diamagnetic correction of 236 x 10^{-6} c.g.s. was made to χ_m for the calculation of μ_{eff}.

bility (uncorrected) was found to be nearly linear in (1/T), over the temperature range 148-300°K the least-squares straight line being $10^4\chi_M = 1221/T + 1.06$. The positive intercept might be taken to indicate the presence of a species with large TIP, although it seems to us rather more likely that, in the temperature range covered, the susceptibility is fortuitously linear in 1/T. Below 148°K the susceptibility dropped below the linear behaviour suggesting species with some sort of exchange between magnetic centres.

The chromatographed M and unchromatographed D samples showed lower susceptibilities at all temperatures, but the temperature variation of $\mu_{eff.}$ was insignificant. The very small magnetic pulls on these samples render the data over much of the temperature range susceptible to relatively large random errors, and the most that one can conclude is that, on the basis of spin-only magnetic moments the number of unpaired electrons in these samples is less than one for every six manganese atoms. If the paramagnetism were due to impurities, as suggested by Basolo and Wawersik,[5] which contained spin-free manganese(II) with a moment of 5.9 B.M., then only about one manganese atom in seventy would have to be paramagnetic to explain the observed susceptibilities.

Attempts were made to measure the susceptibilities in *p*-xylene solution of chromatographed M and D, using the n.m.r. method[10] in order to obtain data under the same conditions as used for the molecular weights. In neither case was any splitting of the methyl proton signal observed, indicating the absence of paramagnetic materials in solution.

The e.s.r. spectra of all samples were run in the solid state and as frozen solutions in benzene, xylene and methanol. It was possible to obtain signals in all cases. The pure solids gave a broad, structureless line about 600 gauss wide, with the exception of diarsMn(CO)$_3$, which gave a resolved structure even in the pure state. The frozen solutions (90°K) showed up the hyperfine structure in all cases, although resolution was not complete for samples M. The spectra consisted of a pattern of six equally intense lines centred on a g-value of 2.000±0.007. The six lines were interspersed with five weak doublets. In Table IV the spacings of the lines are shown, working from low to high fields. The spacings are compared with those of diarsMn(CO)$_3$ and of a frozen methanol solution of manganese(II) acetate. The spectrum of the Mn^{II} species arises from a state S = 5/2. Because of zero-field splitting only the transition $M_s = -\frac{1}{2} \rightarrow +\frac{1}{2}$ is observed,[11] which is split into six components by coupling with the manganese nucleus (I = 5/2). The Mn^0 species, with a d^7 configuration, and S = ½, also shows a single line split by hyperfine interaction into six components. The doublets are thought to be forbidden transitions where the nuclear quantum number M_I changes by ±1. The situation thus occurs where it is not possible to distinguish a spin-free d^5 species from a spin-paired d^7 one.

Table IV. Thc E.S.R. Spectral Hyperfine Splittings.

Products	M	D	diarsMn(CO)$_3$	Mn(ac)$_2$
Main line splitting	88	88	80	90
(gauss)	88	94	80	95
	94	91	80	95
	100	95	80	93
	100	100	100	96
Mean splitting	94	92	84	93
Doublet splitting	unobserved	25	22	25
(gauss)	»	22	22	20
	»	25	24	23
	»	26	25	25
	»	unobserved	unobserved	27

The thermal reaction of a 2:1 triphenylphosphine: manganese carbonyl mixture in *p*-xylene was carried out in the e.s.r. cavity using a sample tube attached to a 300 ml bulb. Before starting the experiment, the apparatus was evacuated and sealed. The bulb allowed carbon monoxide to escape from the sample without building up too much pressure. The tube was heated at 120°C and every forty minutes was frozen in liquid nitrogen and the e.s.r. spectrum recorded. The relative paramagnetism was obtained by measuring the total peak area; the plot of this quantity against time is shown in Figure 3.

A similar experiment was tried using a solvent-free mixture of the reactants as in reactions (c) and (d), but the evolution of carbon monoxide pushed the sam-

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(11) B. T. Allen and D. W. Nebert, *J. Chem. Phys.*, *41*, 1983 (1964)

ple up the tube out of the cavity region.

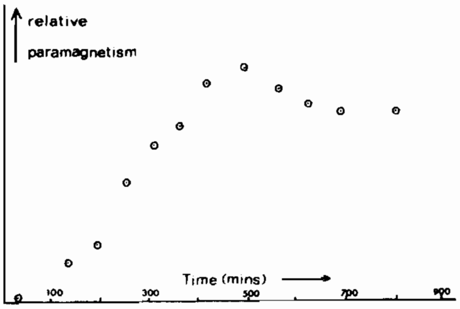

Figure 3. Intensity of the Electron Spin Resonance Signal *vs*. Time, for the $Ph_3P/Mn_2(CO)_{10}$ Reaction Mixture.

Infrared and Mass Spectra. Mass spectra measured on M and D samples showed peaks due only to breakdown of triphenylphosphine when the probe temperature was below 200°C. The highest mass peak was due to PPh_3^+. At temperatures above 200°C however heavier ions appeared. Both M and D species gave spectra very similar to that previously reported by Manning *et al.*,[12] and assumed to be for the binuclear species.

Table V. The Infrared Spectra (cm^{-1}) of M and D in the C—O Stretching Region, in CS_2 solution.

	M	D		
		This work	Ref. 13	
		1895 (4)	1892 (sh)	^{13}CO
		1915 (5)	1913 (sh)	e_3
			1918 (sh)	—
		1934 (sh)	1933 (sh)	—
	1943 (sh)			
e	1953 (100)	1956 (100)	1954 (100)	e_1
		1960 (sh)		
	1974 (9)	1975 (37)	1972 (10)	e_2
	1982 (10)	1982 (35)	1983 (10)	b_2
		2057 (3)	2055 (1)	a_1

Relative intensities are shown in parentheses.

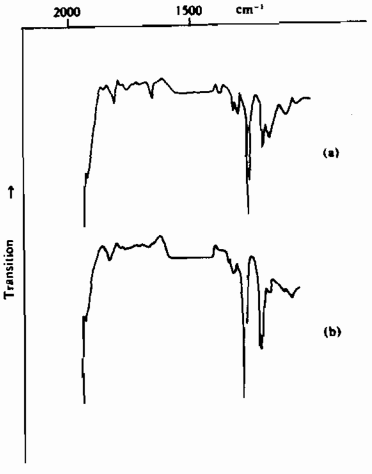

Figure 4. Infrared Spectrum of M (a) Before and (b) After Recrystallisation from $(CD_3)_2CO$.

The infrared spectra of M and D in the C—O stretching region are shown in Table V, together with a literature spectrum.[13] All the spectra are closely similar.

Figure 4 shows the spectra obtained before and after recrystallising M from perdeuteroacetone.

Discussion

Examination of the data reported here shows that the only clear-cut distinction between the two types of sample, M and D, isolated after chromatographic purification, is in their molecular weights in solution. They both appear to be diamagnetic in solution and in the solid state. The fact that e.s.r. signals can be detected indicates the presence of a small amount of paramagnetic impurity. The nature of D is well-known to be 9:10–$(Ph_3P)_2Mn_2(CO)_8$. It is however rather difficult to account for the diamagnetism of M.

The infrared spectrum of M is quite different from that of *cis*–$H(Ph_3P)Mn(CO)_4$.[8] In order to check on the possibility of a hydrogen atom being bonded directly to the manganese in M, the proton n.m.r. spectrum was measured, but no high-field signal obtained. This evidence does not prove the absence of a Mn–H bond, for several reasons. *cis*–$H(Ph_3P)Mn(CO)_4$ and *cis*–$H(Bu_3P)Mn(CO)_4$ were prepared, and it proved impossible to detect high-field signals in these known hydrides also. The absence of the signals could be due to low solubility, quadrupole relaxation, weakening of the signal due to hyperfine spliting by the manganese nucleus, or, rather unlikely, the signal may be in a low-field region and overshadowed by signals from the benzene ring. For these reasons it is felt that a formulation for M as *trans*–$H(Ph_3P)Mn(CO)_4$ may not be incorrect.

Supporting evidence for this structure can be gleaned from the infrared spectra. The *trans*-hydride would be expected to show three C—O stretching frequencies on the basis of C_{4v} symmetry, of species a_1, b_1 and e. The e mode would be intense in infrared absorption, a_1, the totally symmetric stretch, weak because of the nearly planar disposition of the four carbonyl groups, and the b_1 mode would be expected to show up as a fairly weak band because of the phosphine lowering the effective symmetry. One might also expect to see a ^{13}CO band, due to $H(Ph_3P)Mn(^{12}CO)_3(^{13}CO)$, at a frequency below that of the e mode. Qualitatively the observed spectrum fits this description very well, but the small separation between the two high-frequency weak bands makes it unlikely that these are the a_1 and b_1 modes. By comparison with the spectrum of D[13] and with its analysis, the a_1 mode of M would be expected to lie around 2020 cm^{-1}.

The spectra in Figure 4 show that a weak band at 1646 cm^{-1} moves to 1200 cm^{-1} after recrystallising M from perdeuteroacetone. The ratio of these frequencies is 1.37, suggesting very strongly that the 1646 cm^{-1} band is a Mn–H stretching frequency.

The mass spectrum of M shows peaks due to spe-

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(12) J. Lewis, A. R. Manning, J. R. Miller, and J. M. Wilson, *J. Chem. Soc. (A)*, 1663 (1966).

(13) J. Lewis, A. R. Manning, and J. R. Miller, *J. Chem. Soc. (A)*, 845 (1966).

cies such as $[Ph_3PMn_2(CO)_4]^+$. The spectrum could be observed only after heating the probe to 200°C and it seems reasonable to suppose that at these temperatures M dimerises with loss of hydrogen. The ion $[Ph_3PMn(CO)_4]^+$ is present in quite high abundance in the spectra of both M and D, but a molecular ion of M was not detected.

The existence of paramagnetic species during the reaction of triphenylphosphine and manganese carbonyl is demonstrated by the e.s.r. spectra used to follow the reaction. It has not been possible to isolate a paramagnetic compound or to determine whether the paramagnetism is due to a genuine Mn^0 species or to impurities. However, the fact that, at 120°C, the paramagnetism reaches a maximum only after eight hours might explain why Osborne and Stiddard[2] obtained only binuclear samples whereas Hieber and Freyer obtained paramagnetic ones. The former group of authors heated for only four hours, whereas the latter heated the reaction for 16 hours.

Basolo and Wawersik[5] suggested a reaction scheme which explained paramagnetism but did not include the *trans*-hybride. We would suggest that the following reaction sequence might account for the varying reports on this experiment:

1. $Mn_2(CO)_{10} + PPh_3 \rightarrow Mn_2(CO)_9PPh_3 + CO$
2. $Mn_2(CO)_9PPh_3 + PPh_3 \rightarrow (9:10)(PPh_3)_2Mn_2(CO)_8 + CO$
3. $(PPh_3)_2Mn_2(CO)_8 + [H] \rightarrow PPh_3Mn(CO)_4 + H(PPh_3)Mn(CO)_4$
4. $PPh_3Mn(CO)_4 + [H] \rightarrow H(PPh_3)Mn(CO)_4$
5. $H(Ph_3P)Mn(CO)_4 + PH_3P \rightarrow H(Ph_3P)_2Mn(CO)_3 + CO$

where [H] denotes hydrogen abstracted from either the solvent or triphenylphosphine. Basolo and Wawersik's impurities should also be included:

6. $(Ph_3P)_2Mn_2(CO)_8 \rightarrow (Ph_3P)Mn_2(CO)_9$ + paramagnetic impurities.

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