Metal Carbonyl Chemistry. Part 28.[1] Reactions of Decacarbonyldimanganese with Trimethylolpropane Phosphite †

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Thermal reactions of $[Mn_2(CO)_{10}]$ with the sterically constrained ligand $P(OCH_2)_3CEt$ (L) produce the complexes $[Mn_2(CO)_9L]$, $[Mn_2(CO)_8L_2]$, $[Mn_2(CO)_7L_3]$, and $[Mn_2(CO)_6L_4]$. The last compound can also be prepared from either $[Mn_2(CO)_8L_2]$ or $[Mn_2(CO)_7L_3]$ by reaction with L in the appropriate stoicheiometric quantities. All four substitution products are mixtures of isomers arising from substitution in both the axial and equatorial positions. The hydrides *mer-trans*-$[MnH(CO)_3L_2]$, *mer*-$[MnH(CO)_2L_3]$, and *trans*-$[MnH(CO)_2L_3]$ have been obtained in low yield by heating $[Mn_2(CO)_6L_4]$ in xylene solvents. Infrared and ^1H n.m.r. data for all the complexes are discussed.

SUBSTITUTION reactions of decacarbonyldimanganese with tertiary unidentate phosphorus and arsenic ligands give a variety of mono-[2—8] or di-substitution[2—4,6,8,9—22] products with retention of the metal–metal bond. There have been few reports of trisubstitution products of the type $[Mn_2(CO)_7L_3]$ where L is a unidentate ligand.[8,16,22] Under certain conditions homolytic scission of the metal–metal bond can lead to paramagnetic monomeric species,[2,11,15,23] and, in some cases, substituted hydridomanganese carbonyls.[11,15,21,23] Of particular interest in these reactions is the position of substitution in the $[Mn_2(CO)_{10}]$ molecule. So, for example, nitrogen ligands such as aliphatic nitriles and pyridine,[5] the arsine ligands $AsMe_2Ph$, $AsMe_3$, and $AsEt_3$,[21] and PH_3[24] substitute preferentially in an equatorial position, whereas $AsPh_3$, phosphine, and phosphite ligands invariably give axially substituted isomers.[21] It has been argued that the position of substitution is governed by the size of the attacking ligand, and that, although equatorial substitution is favoured both statistically and kinetically, axial substitution is favoured on thermodynamic grounds. In this respect it was of interest to examine the substitution pattern obtained with the sterically constrained phosphite ligand, $P(OCH_2)_3CEt$, which, with the exception of PH_3 and possibly $PPhH_2$, is the smallest trivalent phosphorus ligand available. The results of this investigation are now presented.

RESULTS AND DISCUSSION

Ultraviolet irradiation of a solution of $[Mn_2(CO)_{10}]$ and a two molar excess of $P(OCH_2)_3CEt$ in cyclohexane for 24 h gave a complex mixture of products from which only the tetrasubstituted derivative $[Mn_2(CO)_6\{P(OCH_2)_3CEt\}_4]$ could be isolated in low yield. Better yields and control of the substitution products was achieved by heating mixtures of $[Mn_2(CO)_{10}]$ and the phosphite in *p*-xylene solvent under reflux and with an atmosphere of nitrogen, either in diffuse daylight, or in the absence of light. These ' open-system ' conditions produced much better yields than those carried out at similar temperatures in evacuated, sealed, glass tubes. So, for example, a mixture of $[Mn_2(CO)_{10}]$ and $P(OCH_2)_3CEt$ (1 : 4 mol ratio) in *p*-xylene heated in a sealed tube at 110 °C for 80 h gave only an 8% yield of $[Mn_2(CO)_9\{P(OCH_2)_3CEt\}]$. This compares with the reaction of a 1 : 2 mol ratio of $[Mn_2(CO)_{10}]$ to phosphite ligand in *p*-xylene heated in an ' open system ' at 135 °C for 1.75 h which gave $[Mn_2(CO)_9\{P(OCH_2)_3CEt\}]$ (14%) and the disubstitution product $[Mn_2(CO)_8\{P(OCH_2)_3CEt\}_2]$ (46%). The latter has also been prepared in 25% yield by heating an equimolar mixture of $[Mn_2(CO)_9\{P(OCH_2)_3CEt\}]$ and $P(OCH_2)_3CEt$ in cyclohexane at 100 °C for 2 h.

A mixture of $[Mn_2(CO)_{10}]$ and $P(OCH_2)_3CEt$ (1 : 2.5 mol ratio) heated in *p*-xylene at 135 °C for a longer period (3 h) gave $[Mn_2(CO)_8\{P(OCH_2)_3CEt\}_2]$ (46%) and a trisubstitution product $[Mn_2(CO)_7\{P(OCH_2)_3CEt\}_3]$ (27%). Increasing the carbonyl to ligand ratio to 1 : 5, and lengthening the reaction time to 8 h, resulted in a 15% yield of a tetrasubstituted complex $[Mn_2(CO)_6\{P(OCH_2)_3CEt\}_4]$. Improved yields of this compound were obtained by heating either $[Mn_2(CO)_8\{P(OCH_2)_3CEt\}_2]$ or $[Mn_2(CO)_7\{P(OCH_2)_3CEt\}_3]$ with the phosphite ligand in dioxan at 105 °C over 50 h.

The ^1H n.m.r. spectrum (CH_2Cl_2 solution) of $[Mn_2(CO)_9\{P(OCH_2)_3CEt\}]$ showed two doublets for the OCH_2 hydrogens of the phosphite ligand centred at δ 4.35 [J(P–H) = 5 Hz] and 4.28 [J(P–H) = 5 Hz] in the ratio *ca.* 2 : 1. A similar n.m.r. spectrum was obtained from a solution in benzene, showing that no disproportionation to $[Mn_2(CO)_{10}]$ and $[Mn_2(CO)_8\{P(OCH_2)_3CEt\}_2]$ occurred. A molecular-weight determination in the same solvent indicated that there was no appreciable dissociation of the free ligand. It is concluded from the n.m.r. data that the product is a mixture of axially and equatorially substituted isomers. The carbonyl i.r. spectrum (see Table) can also be explained in terms of overlap of the five bands [2 095m (A_1), 2 020m (A_1), 1 995vs (E), 1 980m (A_1), and 1 965m (E) cm^{-1}] expected for C_{4v} symmetry and axial substitution,[20,21] with the six bands [2 095w (A'), 2 020s (A'), 1 995s ($A' + A''$), 1 980s (A'), 1 965m (A'), and 1 930m (A'') cm^{-1}] expected for C_s symmetry and equatorial substitution.[5] From the relative intensities of these bands it would appear that the axial isomer is the major product, although it is difficult to be certain of this from the available data. Repeated chromatography not only failed to separate these isomers, but also failed to produce any significant change in the relative intensities of the ν(CO) bands.

The complex $[Mn_2(CO)_8\{P(OCH_2)_3CEt\}_2]$ is also

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† 4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane.

obtained as a mixture of two isomers as indicated by the ^{1}H n.m.r. spectrum (CH_2Cl_2 solution). This shows two doublets for the OCH_2 hydrogens of the phosphite ligand centred at δ 4.30 [J(P–H) = 5 Hz] and 4.25 [J(P–H) = 5 Hz] in the ratio *ca.* 2 : 1. This is confirmed by the pattern of bands in the metal-carbonyl region of the i.r. spectrum (see Table), which is far too complex for the one weak and one very strong band normally observed for the diaxially substituted species (D_{4d} symmetry),[21] and shows significant differences in relative intensities from the five bands expected for a diequatorial isomer (C_{2h} symmetry).[21] It seems probable that the major isomer present has the diaxial structure [ν(CO) bands at 2 005w (B_2) and 1 978vs (E_1) cm^{-1}], and is mixed with the diequatorial isomer [ν(CO) bands at 2 073w, 2 005s, 1 978s, 1 955m, and 1 940m cm^{-1}], although the possibility that the second isomer has axial–equatorial substituents cannot be entirely excluded. Since the i.r. spectra of samples of the product mixture taken before and after chromatography show no essential differences, and are identical to the solution spectrum of a sample prepared by thermal decomposition of the corresponding hydride [$MnH(CO)_4\{P(OCH_2)_3CEt\}$],[25] there is a strong possibility that in solution the two isomers exist in equilibrium.

Analytical (%) and i.r. spectroscopic data (cm^{-1}) for the compounds [$Mn_2(CO)_n\{P(OCH_2)_3CEt\}_{10-n}$]

	M.p.	Analysis [a]				
Complex	(θ_c/°C)	C	H	P	M	C–O Stretching frequencies
[$Mn_2(CO)_9\{P(OCH_2)_3CEt\}$]	170—172	34.8 (34.4)	2.2 (2.1)		525 (524) [b]	2 094w, 2 020m–s, 1 995vs, 1 980m, 1 965m, 1 930w (sh) [c]
[$Mn_2(CO)_8\{P(OCH_2)_3CEt\}_2$]	*ca.* 300 [d]	36.5 (36.5)	3.6 (3.3)	9.1 (9.4)		2 073w, 2 005m, 1 978s, 1 955m, 1 940w–m [e]
[$Mn_2(CO)_7\{P(OCH_2)_3CEt\}_3$]	250 [d]	38.1 (37.9)	3.9 (4.2)	11.4 (11.7)		2 075w, 2 058w, 2 052w, 2 007m, 1 980s, 1 968s, 1 955m (sh), 1 942w–m (sh), 1 925w–m [f]
[$Mn_2(CO)_6\{P(OCH_2)_3CEt\}_4$]	*ca.* 200 [d]	38.5 (38.8)	4.8 (4.8)		944 (926) [g]	2 070w, 2 055w, 2 005w, 1 977s, 1 965s, 1 950s, 1 920m [f]

[a] Calculated values are given in parentheses. [b] In benzene. [c] In cyclohexane. [d] With decomposition. [e] In CS_2. [f] In *p*-xylene. [g] In 1,2-dichloroethane.

The ^{1}H n.m.r. spectrum (acetone solution) of an analytically pure sample of [$Mn_2(CO)_7\{P(OCH_2)_3CEt\}_3$] showed two overlapping doublets centred at δ 4.30 [J(P–H) = 5 Hz] and 4.24 [J(P–H) = 5 Hz] and a well resolved apparent 1 : 2 : 1 triplet centred at δ 4.12 [J(P–H) = 5 Hz] * for the OCH_2 hydrogens of the ligand. In addition there were two other, much weaker, peaks at δ 4.16 and 4.06, which are probably part of two other doublets. The product is obviously a mixture of at least two isomers, but it is impossible to distinguish between the isomers (1)—(6) on the basis of the n.m.r. spectrum. The 1 : 2 : 1 apparent triplet which arises by virtual coupling of two phosphite ligands is not diagnostic, since both *cis*- and *trans*-phosphorus ligands are known to give rise to strong P–P coupling.[21,26,27] A study of the metal-carbonyl i.r. spectrum (see Table) before and after chromatography indicated that partial separation of the isomers could be achieved. One isomer appeared to have bands at 2 058w, 2 052w, 1 965vs, and 1 925m–s cm^{-1}. The simplicity of the spectrum suggests that this compound probably has structure (1), as all the other structures might be expected to exhibit a greater number of intense bands. The other component of the mixture had bands at 2 075w, 2 007m–s, 1 980vs, 1 955s, and 1 942m–s cm^{-1}, but it is impossible to obtain any structural information from this pattern since all the remaining isomers (2)—(6) could account for the bands observed. The possibility that this trisubstituted derivative may be a mixture of [$Mn_2(CO)_6\{P(OCH_2)_3CEt\}_4$] and [$Mn_2(CO)_8\{P(OCH_2)_3CEt\}_2$] was also investigated, but major differences in solubilities and behaviour under chromatographic conditions made this untenable.

The ^{1}H n.m.r. spectrum (acetone solution) of the tetrasubstituted derivative [$Mn_2(CO)_6\{P(OCH_2)_3CEt\}_4$] in the OCH_2 region showed a doublet centred at δ 4.27 [J(P–H) = 5 Hz] and a well resolved, apparent triplet at δ 4.14 [J(P–H) = 5 Hz] * in the intensity ratio *ca.* 4 : 7. Repeated chromatography gave partial separation of the product into isomers, and from the i.r. spectrum (see Table) one isomer appears to have ν(CO) bands at 2 055w, 1 965vs, and possibly a strong shoulder at *ca.* 1 950 cm^{-1}, which is in good agreement with that expected for a structure (7) rather than an isomer such as (8) predicted on steric grounds. Structure (8), and indeed any other possible structure other than (7), would undoubtedly give a much more complex pattern in the i.r. spectrum, such as that observed for the other component of the mixture, which has bands at 2 070w, 2 050w, 2 005m, 1 977vs, 1 950vs, and 1 920m cm^{-1}.

It is interesting that in both [$Mn_2(CO)_7\{P(OCH_2)_3CEt\}_3$] and [$Mn_2(CO)_6\{P(OCH_2)_3CEt\}_4$] one of the main isomers formed in each case appears to have *trans*-equatorial substituents, rather than the *cis* isomers predicted on kinetic considerations. It has been noted previously, however, that isomers of the type *fac*-[$MnX(CO)_3L_2$] [X = OCPh, L = $P(OCH_2)_3CEt$;[28] X = Cl or Br, L = $PPh(OMe)_2$[29]] readily isomerise to the corresponding *mer-trans* isomers, and this may account for the *trans* isomers.

It is apparent from these results that the degree of

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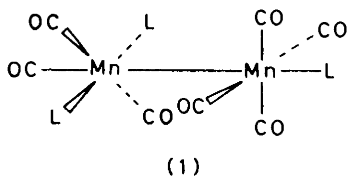
* J(P–H) in this case refers to the separation of the two outside lines of the triplet.

polysubstitution and the extent of substitution in equatorial positions is far greater with the ligand $P(OCH_2)_3CEt$ than with any other phosphine or phosphite ligand. It might be argued that this constrained phosphite ligand represents a ligand which is intermediate between those which give purely axially substituted mono- and di-ligand complexes, and those which afford only equatorially substituted derivatives. Elegant work by Brown and co-workers [22,23] and by Poë and co-workers [12,13,20] has produced substantial evidence that under both thermal and photochemical conditions substitution in $[Mn_2(CO)_{10}]$ occurs by initial homolysis of the weak Mn–Mn bond. The resultant radical $[Mn(CO)_5]$, which is probably best considered as a six-co-ordinate species with the unpaired electron occupying a co-ordination position,[22] is remarkably labile towards substitution of one of the CO ligands. It has been argued convincingly [22] that the unpaired electron will labilise the *cis*-carbonyl ligands more than the *trans*-carbonyl leading to the radical *cis*-$[Mn(CO)_4L]$. It follows from this that the stereochemistry of the dimer products $[Mn_2(CO)_8L_2]$ isolated from these reactions will depend upon a competition between radical dimerisation (k_d) and radical isomerisation (k_i) as shown in the Scheme.



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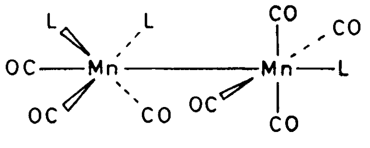

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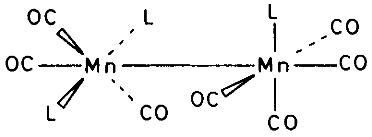

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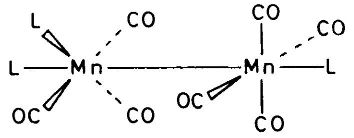

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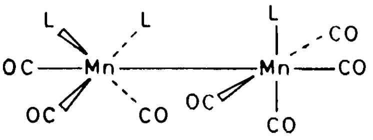

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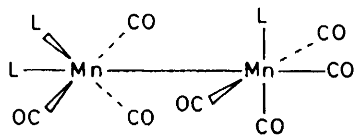

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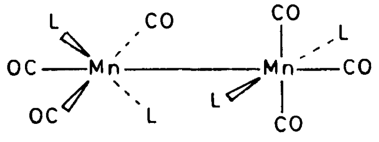

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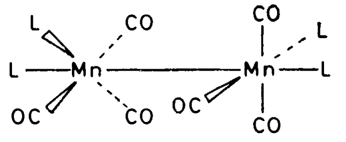
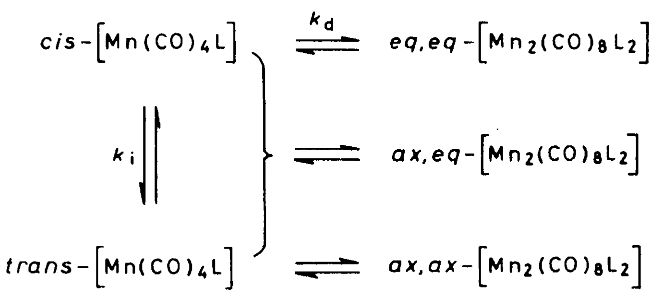


(8)

When L is relatively small then k_d might be expected to be greater than k_i, but as the size of L increases then k_i, and hence dimerisation of *trans*-$[Mn(CO)_4L]$ to *ax,ax*-$[Mn_2(CO)_8L_2]$ and/or *ax,eq*-$[Mn_2(CO)_8L_2]$, becomes comparable and eventually greater than k_d. A useful indication of the size of a ligand is given by the ligand cone angle θ as defined by Tolman.[30] Model measurements indicate that the ligand $P(OCH_2)_3CEt$ has a cone angle of 101°. This is rather smaller than that of PF_3 ($\theta = 104°$), which gives only axial mono- and di-substitution products,[6] but larger than those of the ligands PH_3 ($\theta = 87°$) and RCN ($\theta \sim 95°$) which afford equatorial substitution products exclusively.[5,24] Thus, it would appear that if a radical mechanism is operating in all these reactions for the radical *cis*-$[Mn(CO)_4\{P(OCH_2)_3CEt\}]$, k_d is of the same order of magnitude as k_i. A difficulty arises on consideration of the arsine ligands $AsMe_2Ph$, $AsMe_3$, and $AsEt_3$ which have been shown to produce only diequatorial substitution products under u.v. conditions.[21] The Mn–As distance (2.46 Å) in *eq,eq*-$[\{Mn(CO)_4(AsMePh_2)\}_2]$ is only 0.23 Å longer than the corresponding Mn–P distance (2.23 Å) in $[\{Mn(CO)_4(PMePh_2)\}_2]$.[7] This might be expected to reduce the cone angle of the arsine ligand by *ca.* 10° compared with that of the phosphine ligand, and assuming a similar reduction for the other arsine ligands this would result in cone angles of *ca.* 108 ($AsMe_3$), 112 ($AsMe_2Ph$), and 126° ($AsMePh_2$).[30] These values are all in excess of the cone angles of the ligands PF_3, $P(OMe)_3$, and $P(OEt)_3$ which produce axial substitution products exclusively, and are very much larger than the cone angle of $P(OCH_2)_3CEt$, which, as demonstrated in this work, gives some axial substitution. Further investigation of these reactions of arsine ligands seems warranted. However, it must be accepted that, in the absence of reliable data about the rates of isomerisation of the species $[Mn_2(CO)_9L]$, $[Mn_2(CO)_8L_2]$, $[Mn_2(CO)_7L_3]$, and $[Mn_2(CO)_6L_4]$ in solution, then mechanistic conclusions drawn from the degree of axial *versus* equatorial substitution must remain speculative.



SCHEME

In none of the reactions of $[Mn_2(CO)_{10}]$ with $P(OCH_2)_3CEt$ was there any evidence for the formation of paramagnetic or hydride complexes. This cannot be taken as evidence against a homolytic mechanism, but probably indicates that the radical combination and isomerisation reactions occur at a fast rate, and certainly faster than H-atom abstraction from a solvent molecule. Prolonged heating of a solution of $[Mn_2(CO)_6\{P(OCH_2)_3CEt\}_4]$ in either *p*- or *m*-xylene at 140 °C over 70 h in the dark resulted in appreciable decomposition and gave a small quantity of *trans*-$[MnH(CO)_3\{P(OCH_2)_3CEt\}_2]$ [25] among the products. Under less severe conditions, *i.e.* heating a *m*-xylene solution at 135 °C for 45 h in diffuse daylight, the hydride $[MnH(CO)_2\{P(OCH_2)_3CEt\}_3]$ [25] was isolated from the reaction mixture. In solution this exists as an equilibrium between the *mer* and the *trans* isomers. It is not unreasonable to suppose that for a radical such as $[Mn(CO)_3\{P(OCH_2)_3CEt\}_2]$ the rate of recombination will be slower than for a radical such as $[Mn(CO)_4\{P(OCH_2)_3CEt\}]$, and alternative reactions such as H-atom abstraction and further CO-ligand substitution are more competitive. Our failure to isolate any products of type $[Mn_2(CO)_4\{P(OCH_2)_3CEt\}_6]$ or $[Mn_2(CO)_5\{P(OCH_2)_3CEt\}_5]$ suggests a radical such as $[Mn(CO)_2\{P(OCH_2)_3CEt\}_3]$ is unreactive towards dimerisation.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer model 257 spectrophotometer, ^1H n.m.r. spectra on a Varian HA 100 instrument at 100 MHz using tetramethylsilane as internal reference. Molecular weights were determined using a Mechrolab vapour-pressure osmometer.

Decacarbonyldimanganese was prepared by the atmospheric pressure carbonylation of a mixture of tricarbonyl-(methylcyclopentadienyl)manganese and sodium,[31] and trimethylolpropane phosphite was prepared by a reported procedure.[32] All reactions and purification procedures were carried out under an atmosphere of nitrogen, and chromatographic separations were carried out with a column of deactivated alumina (30 × 1.8 cm).

Nonacarbonyl(trimethylolpropane phosphite)dimanganese and Octacarbonylbis(trimethylolpropane phosphite)dimanganese.—A solution of phosphite (7.5 g, 46.3 mmol) in *p*-xylene (15 cm^3) was added over a period of 1 h to a refluxing solution of $[Mn_2(CO)_{10}]$ (8.4 g, 21.5 mmol) in *p*-xylene (15 cm^3). On completion of the addition the mixture was refluxed for another 45 min before cooling. The solid which precipitated was chromatographed using diethyl ether as eluant to give yellow crystals of $[Mn_2(CO)_9\{P(OCH_2)_3CEt\}]$ (1.5 g, 2.8 mmol, 14%), purified by repeated chromatography. The use of acetone as eluant gave light yellow crystals of $[Mn_2(CO)_8\{P(OCH_2)_3CEt\}_2]$ (6.6 g, 10.0 mmol, 47%) purified by recrystallisation from acetone–water (15 : 1).

Octacarbonylbis(trimethylolpropane phosphite)dimanganese from $[Mn_2(CO)_9\{P(OCH_2)_3CEt\}]$.—The phosphite (0.2 g, 1.2 mmol) and $[Mn_2(CO)_9\{P(OCH_2)_3CEt\}]$ (0.5 g, 1.0 mmol) in cyclohexane (50 cm^3) were heated in a sealed tube at 100 °C for 24 h to give $[Mn_2(CO)_8\{P(OCH_2)_3CEt\}_2]$ (0.15 g, 0.25 mmol, 25%).

Heptacarbonyltris(trimethylolpropane phosphite)dimanganese.—Addition of a solution of phosphite (8.1 g, 50 mmol) in *p*-xylene (15 cm^3) over a period of 15 min to a refluxing solution of $[Mn_2(CO)_{10}]$ (7.6 g, 19.5 mmol) in *p*-xylene (15 cm^3), followed by further reflux for 2.75 h, gave a solid on cooling. This was chromatographed using light petroleum, benzene, and acetone as eluants. The benzene fraction contained $[Mn_2(CO)_8\{P(OCH_2)_3CEt\}_2]$ (3.5 g, 5.3 mmol, 27%), while the acetone fraction gave yellow crystals of $[Mn_2(CO)_7\{P(OCH_2)_3CEt\}_3]$ (7.0 g, 9.0 mmol, 46%).

Hexacarbonyltetrakis(trimethylolpropane phosphite)dimanganese.—(*a*) *From* $[Mn_2(CO)_{10}]$. A solution of phosphite (8.8 g, 54.3 mmol) in *p*-xylene (15 cm^3) was added to a refluxing solution of $[Mn_2(CO)_{10}]$ (3.6 g, 9.2 mmol) in *p*-xylene (20 cm^3) over 2.5 h, and the mixture was refluxed for another 5.5 h to give an orange solid. This, on chromatography (diethyl ether eluant), gave orange-yellow crystals of $[Mn_2(CO)_6\{P(OCH_2)_3CEt\}_4]$ (1.2 g, 1.4 mmol, 15%).

(*b*) *From* $[Mn_2(CO)_8\{P(OCH_2)_3CEt\}_2]$. A solution of $[Mn_2(CO)_8\{P(OCH_2)_3CEt\}_2]$ (1.2 g, 1.8 mmol) and phosphite (0.7 g, 5.0 mmol) in dioxan (25 cm^3) was heated in a Pyrex tube, sealed under vacuum, for 50 h at 105 °C. The yellow solid which precipitated on cooling was chromatographed (ether eluant) to give $[Mn_2(CO)_6\{P(OCH_2)_3CEt\}_4]$ (0.91 g, 0.98 mmol, 54%).

(*c*) *From* $[Mn_2(CO)_7\{P(OCH_2)_3CEt\}_3]$. The phosphite (1.0 g, 6.2 mmol) and $[Mn_2(CO)_7\{P(OCH_2)_3CEt\}_3]$ (2.0 g, 2.5 mmol) in dioxan (50 cm^3) heated in a sealed tube at 100 °C for 50 h gave $[Mn_2(CO)_6\{P(OCH_2)_3CEt\}_4]$ (0.7 g, 0.75 mmol, 30%) after reducing the volume of the solvent and addition of light petroleum.

Thermolysis of $[Mn_2(CO)_6\{P(OCH_2)_3CEt\}_4]$ *in Xylene.*—When a solution of $[Mn_2(CO)_6\{P(OCH_2)_3CEt\}_4]$ (0.1 g, 0.1 mmol) in *m*-xylene (10 cm^3) was gently refluxed for 45 h, filtration of the solution while hot followed by addition of light petroleum caused precipitation of white crystals of $[MnH(CO)_2\{P(OCH_2)_3CEt\}_3]$ (0.02 g, 0.04 mmol, 20%). When this reaction was repeated using $[Mn_2(CO)_6\{P(OCH_2)_3CEt\}_4]$ (0.1 g, 0.1 mmol) in *p*-xylene (5 cm^3) heated in a sealed tube for 70 h at 140 °C, the yellow precipate formed on addition of light petroleum was shown by i.r. spectroscopy to be a mixture of starting material and decomposition products containing a small quantity of *trans*-[$MnH(CO)_3$-{$P(OCH_2)_3CEt$}$_3$].

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