Metal Carbonyl Chemistry. Part 29.[1] Preparation and Properties of the Hydrides $[MnH(CO)_{5-n}\{P(OCH_2)_3CEt\}_n]$ (n = 1, 2, or 3) †

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The hydrides *cis*-$[MnH(CO)_4L]$, *mer-trans*-$[MnH(CO)_3L_2]$, *mer-trans*-$[MnH(CO)_3(PPh_3)L]$, and *mer-trans*- and *mer-cis*-$[MnH(CO)_2L_3]$ [L = $P(OCH_2)_3CEt$] have been prepared by stepwise substitution of the carbonyl ligands in $[MnH(CO)_5]$. The corresponding deuterides *mer-trans*-$[MnD(CO)_3L_2]$ and *mer-trans*-$[MnD(CO)_2L_3]$ have also been synthesised by substitution in *cis*-$[MnD(CO)_4L]$, obtained from the reaction between $Na[Mn(CO)_4L]$ and DCl. Infrared and ^1H n.m.r. spectroscopy have shown that while the mono- and bis-phosphite ligand-substituted complexes do not isomerise to any appreciable extent, the compounds $[MnX(CO)_2L_3]$ (X = H or D) exist as a *ca.* 1 : 1 equilibrium mixture of the *mer-trans* and *mer-cis* isomers in solution, and on warming above 100 °C in the solid state the pure *mer-cis* isomer is converted smoothly into the *mer-trans* isomer. Heating $[MnH(CO)_4L]$ in solution gives either $[\{Mn(CO)_4L\}_2]$ or $[MnCl(CO)_4L]$ depending on whether hydrocarbon or chlorinated solvents are used.

PREVIOUS studies on the substitution reactions of pentacarbonylhydridomanganese with unidentate tertiary phosphine and phosphite ligands have shown that monosubstitution leads to either *cis*-$[MnH(CO)_4L]$ [when L = PPh_3 [2,3] or $P(OPh)_3$ [2]] or a mixture of *cis* and *trans* isomers [when L = PF_3 [4] or $P(CF_3)_2X$ (X= CF_3, F, or Me) [5]]. Disubstitution results in the formation of either pure *mer-trans*-$[MnH(CO)_3L_2]$ [when L = PPh_3 [2] or $PMe(OPh)_2$ [2]] or an equilibrium mixture containing mainly the *mer-trans* isomer [when L = $P(OPh)_3$ [2]] together with a small amount of the *fac* isomer, except when L = PF_3 [4] which affords an equilibrium mixture of all three possible isomers. Attempts at further carbonyl substitution have been successful only with PF_3.[4] The degree of substitution and the extent of isomerisation in solution appear to be related to the relative donor strengths of the phosphorus ligands, but steric factors may also play an important role in these reactions. In an effort to gain further insight into the factors which control substitution and isomerisation we have investigated the reaction of $[MnH(CO)_5]$ with the sterically constrained phosphite ligand $P(OCH_2)_3CEt$, and the results of this study are now reported.

RESULTS AND DISCUSSION

Addition of $[MnH(CO)_5]$ to a slight molar excess of $P(OCH_2)_3CEt$ (L) in light petroleum at room temperature gave *cis*-$[MnH(CO)_4L]$ (85% yield) together with traces of *mer-trans*-$[MnH(CO)_3L_2]$ and *mer-cis*- and *mer-trans*-$[MnH(CO)_2L_3]$. The *cis*-monosubstituted complex was also obtained in 75% yield as the only product when an excess of $[MnH(CO)_5]$ was distilled on to the solid phosphite ligand held at 0 °C. An attempt to prepare a sample of the *trans* isomer by acidification of the sodium salt prepared by reduction of the dimer $[\{Mn(CO)_4L\}_2]$, which in solution consists of *ca.* 2 : 1 ratio of the *ax,ax* isomer mixed with either the *eq,eq* or *ax,eq* isomers,[1] gave only *cis*-$[MnH(CO)_4L]$ in 93% (isolated) yield. Acidification of the sodium salt with a 10% solution of DCl in D_2O resulted in an 82% yield of the deuteride *cis*-$[MnD(CO)_4L]$. From a comparison of the i.r. spectra of the hydride and deuteride complexes it was possible [5,6] to assign symmetry labels to the four carbonyl-stretching absorptions ($3A' + A''$) observed for the C_3 symmetry of the *cis* structure (Table 2). The Mn–H stretching absorption, which normally occurs in the region of 1 800 cm^{-1},[7] was too weak to observe above the background absorptions and other minor bands in the spectrum, but with the deuteride a weak band for the Mn–D absorption was observed at 1 290 cm^{-1}; a region which was relatively free of the other bands. The presence of the Mn–H band was established beyond doubt by the doublet at δ −8.5 in the ^1H n.m.r. spectrum (Table 2).

TABLE 1

Melting-point, molecular-weight, and analytical data for the new substituted manganese carbonyl hydrides and deuterides [a]

Complex	M.p. (θ_c/°C)	Analysis (%) [b]	
		C	H
cis-$[MnH(CO)_4L]$ [c]	112	36.6 (36.4)	3.6 (3.6)
cis-$[MnD(CO)_4L]$	105—108	36.9 (36.4)	3.9 (3.6)
mer-trans-$[MnH(CO)_3L_2]$	220 [d]	39.0 (38.8)	5.5 (5.0)
mer-trans-$[MnD(CO)_3L_2]$		38.9 (38.8)	5.3 (5.0)
mer-trans-$[MnH(CO)_3(PPh_3)L]$	250 [d]	56.2 (56.6)	4.8 (4.8)
mer-cis-$[MnH(CO)_2L_3]$ [e]	262—264	40.2 (40.1)	6.0 (5.7)
mer-trans-$[MnH(CO)_2L_3]$	263—265 [d]	40.2 (40.1)	6.0 (5.7)

[a] L = $P(OCH_2)_3CEt$. [b] Calculated values are given in parentheses. [c] P, 9.2 (9.4%). [d] With decomposition. [e] *M* 652 (calc.: 598) in benzene solvent.

When $[MnH(CO)_5]$ was added slowly to a solution of $P(OCH_2)_3CEt$ in *p*-xylene heated at 100 °C the product was *mer-trans*-$[MnH(CO)_3L_2]$ [L = $P(OCH_2)_3CEt$] obtained in 65% yield. The same compound was also produced in 80—85% yield either by reaction of *cis*-$[MnH(CO)_4\{P(OCH_2)_3CEt\}]$ with a slight molar excess of the phosphite ligand at 10 °C in dioxan over 12 h, or by heating an intimately ground mixture of the two solids at 90 °C for 14 h in a tube sealed under vacuum. The reactions carried out in solution were monitored by i.r. spectroscopy at regular intervals but there was no evidence for the formation of any product other than the

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† $P(OCH_2)_3CEt$ = 4-Ethyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane.

mer-trans isomer. The corresponding deuteride *mer-trans*-[MnD(CO)$_3$L$_2$] was produced in 86% yield on heating a mixture of *cis*-[MnD(CO)$_4$L] and P(OCH$_2$)$_3$CEt at 90 °C over 14 h. Triphenylphosphine also reacts with *cis*-[MnH(CO)$_4${P(OCH$_2$)$_3$CEt}] in dioxan at room temperature to give *mer-trans*-[MnH(CO)$_3$(PPh$_3$){P(OCH$_2$)$_3$CEt}] in 54% yield. However, *cis*-[MnH(CO)$_4$(PPh$_3$)] failed to react with P(OCH$_2$)$_3$CEt under similar conditions.

The solid-state i.r. spectra of [MnX(CO)$_3$L{P(OCH$_2$)$_3$CEt}] [X = H or D, L = P(OCH$_2$)$_3$CEt; X = H, L = PPh$_3$] (Table 2) showed one weak and two strong bands ($2A_1 + B_1$) in the carbonyl region typical of the C symmetry of a *mer-trans*-substituted molecule,[8] although in the case of [MnH(CO)$_3$(PPh$_3$){P(OCH$_2$)$_3$CEt}] the strong A_1 and B_1 bands were not well resolved. In addition, the spectrum of [MnD(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$] showed a weak absorption at 1 310—1 315 cm^{-1} for the Mn–D bond. The spectrum of a solution of [MnH(CO)$_3$(PPh$_3$){P(OCH$_2$)$_3$CEt}] in CS$_2$ was unchanged from that of the solid, in contrast to the solution spectrum of [MnH(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$] which showed weak bands at 2 030 and 1 930 cm^{-1}, which were not evident in the solid-state spectrum. This may indicate a small degree of isomerism to either the *fac* or *mer-cis* isomer in solution. The *mer-trans* structure of the complex [MnH(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$] was established by the ^{1}H n.m.r. spectrum (Table 2), which showed a symmetrical 1 : 2 : 1 triplet for the hydridic proton arising from equal ^{31}P coupling of the two phosphorus atoms *cis* to the hydride ligand. The *trans* arrangement of the phosphite ligands was confirmed by the apparent 1 : 2 : 1 triplet (X$_6$AA'X'$_6$ pattern) for the OCH$_2$ protons arising by virtual coupling of the two *trans* ^{31}P atoms. An Mn–H signal could not be detected for *mer-trans*-[MnH(CO)$_3$(PPh$_3$){P(OCH$_2$)$_3$CEt}] due to low solubility, but the doublet of doublets pattern for the OCH$_2$ protons is consistent with the assigned structure.

TABLE 2

Infrared (cm^{-1}) and ^{1}H n.m.r. spectroscopic data

Complex	C–O Stretching frequencies [a]				^{1}H N.m.r. data (δ) [b]	
					OCH$_2$	Mn-H
cis-[MnH(CO)$_4$L]	2 080m (A')	2 005s (A'')	1 990s (A')	1 977s (A')	4.28 (d) [J(P–H) 5] [c,d]	−8.5 (d) [J(P–H) 54]
cis-[MnD(CO)$_4$L]	2 080m (A')	2 005s (A'')	1 985s (A')	1 976s (A')	4.35 (d) [J(P–H) 5] [d,e]	
mer-trans-[MnH(CO)$_3$L$_2$]	2 040w (A_1)	1 960s (B_1)	1 940s (A_1)		4.23 (t) [e] [J(P–H) 10] [c,d,f]	−9.3 (t) [J (P–H) 48]
mer-trans-[MnD(CO)$_3$L$_2$]	2 040w (A_1)	1 960s (B_1)	1 940s (A_1)			
mer-trans-[MnH(CO)$_3$(PPh$_3$)L]	2 005w (A_1)	1 915—1 925s, br	($A_1 + B_1$)		4.82 (dd) [J(P–H) 5, J(P'–H) 1] [c,g]	
mer-cis-[MnH(CO)$_2$L$_3$]	1 970s (A')	1 900s (A')			} 4.15 [h]	−9.6 (q) [J(P–H) 54]
mer-trans-[MnH(CO)$_2$L$_3$]	2 000vw (A_1)	1 910s (B_1)				
mer-trans-[MnD(CO)$_2$L$_3$]	2 000vw (A_1)	1 910s (B_1)				

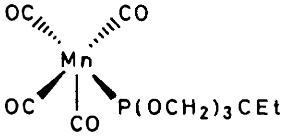
[a] Nujol mulls. [b] d = Doublet, t = triplet, q = quartet, dd = doublet of doublets. J values in Hz. [c] In CH$_2$Cl$_2$ solution. [d] Internal reference is SiMe$_4$. [e] In (CD$_3$)$_2$CO solution. [f] Apparent triplet; J(P–H) refers to separation of the outside lines. [g] Benzene external reference. [h] Broad singlet.

An attempt was made to prepare an alternative isomer *fac*-[MnH(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$] by reduction of *fac*-[MnBr(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$], obtained from [MnBr(CO)$_5$] by reaction with an excess of P(OCH$_2$)$_3$CEt in chloroform under reflux. No reduction was observed with Na[BH$_4$] in tetrahydrofuran at room temperature over 2.5 h, but with Li[AlH$_4$] under similar conditions *mer-trans*-[MnH(CO)$_3$L$_2$] was obtained in 45% yield as the only product.

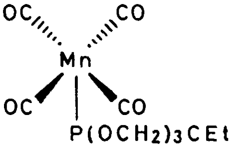
When an intimately ground mixture of *mer-trans*-[MnH(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$] and an excess of P(OCH$_2$)$_3$CEt was heated in a sealed tube at 115 °C for 15 h, removal of the excess of ligand by sublimation gave *mer-trans*-[MnH(CO)$_2${P(OCH$_2$)$_3$CEt}$_3$] in 78% yield. A similar procedure was also employed for the synthesis of *trans*-[MnD(CO)$_2${P(OCH$_2$)$_3$CEt}$_3$] in 80% yield from *trans*-[MnD(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$]. Attempts to recrystallise *mer-trans*-[MnH(CO)$_2${P(OCH$_2$)$_3$CEt}$_3$] by dissolving in hot benzene resulted in quantitative isomerisation to the *mer-cis* isomer. Both the *mer-cis* and the *mer-trans* isomers are stable over a long period at room temperature, but on heating the *mer-cis* derivative above 100 °C in the solid state *in vacuo* it is converted quantitatively and irreversibly, without decomposition, into the *mer-trans* isomer. This explains the apparently identical melting points obtained for the two compounds (see Table 1). When each isomer is dissolved separately in a solvent such as acetone, chloroform, or carbon disulphide, i.r. spectroscopy shows that at room temperature a *ca.* 1 : 1 equilibrium mixture of the *mer-cis* and *mer-trans* isomers is established within the time taken to dissolve the samples. The rate of isomerisation in acetone was too fast to measure at room temperature. The ^{1}H n.m.r. spectrum (Table 2) shows the Mn–H signal as a regular 1 : 3 : 3 : 1 quartet at the mean chemical-shift value of δ −9.6. Attempts at variable-temperature studies were unsuccessful due to poor solubility at lower temperatures. The appearance of the n.m.r. spectrum was unaffected by the presence of up to a 10^4 molar excess of phosphite ligand, suggesting that dissociation of a phosphite molecule is not an important step in this isomerisation reaction, unlike the conversion of *fac*-[MnBr(CO)$_3${P(OPh)$_3$}$_2$] into the *mer-trans* isomer.[9,10] The possibility that rearrangement occurs by cleavage of the manganese–hydrogen bond can also be discounted since *mer-trans*-[MnD(CO)$_2${P(OCH$_2$)$_3$CEt}$_3$] similarly isomerises in acetone solution to give *mer-cis*-[MnD(CO)$_2${P(OCH$_2$)$_3$CEt}$_3$] with no evidence for D–H exchange. Further work is necessary to establish the mechanism of this interesting isomerisation reaction, but the data available to date favour a non-dissociative exchange of an equatorial CO ligand with the axial phosphite ligand *trans* to the hydride ligand, possibly by a twist mechanism as described previously for similar octahedral complexes.[11]

All efforts to prepare the tetrasubstituted hydride $[MnH(CO)\{P(OCH_2)_3CEt\}_4]$ by heating *mer-trans*-$[MnH(CO)_2\{P(OCH_2)_3CEt\}_3]$ with an excess of $P(OCH_2)_3CEt$ both in the presence and absence of solvent at temperatures up to 150 °C invariably resulted in almost quantitative recovery of the starting materials. The lack of reaction is a little surprising in view of the report [10] that further substitution does occur readily in bromo-compounds, *e.g.* *mer-trans*-$[MnBr(CO)_2\{P(OMe)_3\}_3]$.[10]

The compound *cis*-$[MnH(CO)_4\{P(OCH_2)_3CEt\}]$ reacted with CCl_4 at 45 °C over 16 h to give *cis*-$[MnCl(CO)_4\{P(OCH_2)_3CEt\}]$ in 70% yield. A concentrated solution of the same hydride in dioxan on standing for several minutes at room temperature slowly lost hydrogen and began to deposit crystals of a yellow solid having an i.r. spectrum (Nujol mull) with bands at 2 072w, 1 995s, 1 965s,br, 1 945s, 1 920w(sh), and 1 905 cm^{-1} in the metal-carbonyl region consistent with the structure *eq-eq*-$[\{Mn(CO)_4[P(OCH_2)_3CEt]\}_2]$. More dilute dioxan solutions decomposed to give variable yields of *ax,ax*-$[\{Mn(CO)_4[P(OCH_2)_3CEt]\}_2]$, and on heating a toluene solution of the hydride at 95 °C for 43 h a 75% yield of *ax,ax*-$[\{Mn(CO)_4[P(OCH_2)_3CEt]\}_2]$ was obtained. When a similar solution was heated at a higher temperature (110 °C) for a longer period (54 h) the yield of the *ax,ax*-disubstituted dimer decreased to 41% and $[MnH(CO)_3\{P(OCH_2)_3CEt\}_2]$ (16%) was isolated from the reaction. It seems probable that these dimers arise by homolysis of the Mn–H bond followed by coupling of the resultant $[Mn(CO)_4\{P(OCH_2)_3CEt\}]$ radicals. Recent matrix-isolation i.r. spectroscopic studies of the radicals $[Mn(CO)_5]$ [12] and $[Re(CO)_5]$ [13] indicate that they have square-pyramidal structures. The e.s.r. spectra of $[Mn(CO)_3L_2]$ [$L = PBu_3$ or $P(OEt)_3$] have also been reported recently,[14] and are consistent with a square-pyramidal geometry with the phosphorus ligands occupying mutually *trans* basal positions. Similarly, isomeric forms of stable, paramagnetic, phosphine-substituted rhenium carbonyls, such as *trans*-$[Re(CO)_3(PPh_3)_2]$ and *cis*-$[Re(CO)_3(PMePh_2)_2]$, have been known for a number of years.[15-18] It is, therefore, entirely reasonable to suppose that the radical $[Mn(CO)_4\{P(OCH_2)_3CEt\}]$ can have the structure (1) or (2).



(1)



(2)

On heating a concentrated solution of *cis*-$[MnH(CO)_4\{P(OCH_2)_3CEt\}]$ the initially formed radical (1) could dimerise before rearrangement to (2) can occur giving a dimer having the same stereochemistry as the original hydride. Under more dilute conditions, or at higher temperatures, isomerisation of (1) to (2) can occur before dimerisation leading to the *ax,ax*-disubstituted dimer. Above 100 °C appreciable decomposition of the hydride, dimer, or both must occur to give free ligand, and this, on reaction with *cis*-$[MnH(CO)_4\{P(OCH_2)_3CEt\}]$, gives *mer-trans*-$[MnH(CO)_3\{P(OCH_2)_3CEt\}_2]$ which is thermally stable under these conditions.

EXPERIMENTAL

The compounds $[MnH(CO)_5]$ [2] and $P(OCH_2)_3CEt$ [19] were prepared by the published methods. All reactions and purification procedures were carried out under an atmosphere of dry nitrogen, and solvents were deaerated prior to use. Proton n.m.r. spectra were recorded either on a Perkin-Elmer R10 instrument at 60 MHz or on a Varian HA100 instrument at 100 MHz, i.r. spectra on a P.E.257 grating spectrophotometer.

cis-$[MnH(CO)_4\{P(OCH_2)_3CEt\}]$.—(*a*) *From* $[MnH(CO)_5]$ *in a solvent.* Pentacarbonylhydridomanganese (6.0 g, 30.1 mmol) was added over a period of 45 min to a stirred solution of $P(OCH_2)_3CEt$ (6.3 g, 38.9 mmol) in light petroleum (160 cm^3, b.p. 40—60 °C) at room temperature, and stirring was continued for another 3 h to give a white solid which precipitated slowly from solution. This was filtered off and washed with light petroleum to give *cis*-$[MnH(CO)_4\{P(OCH_2)_3CEt\}]$ (8.6 g, 26.1 mmol, 85%). Removal of the solvent from the filtrate gave a small amount of residue shown by i.r. spectroscopy to be a mixture of *cis*-$[MnH(CO)_4\{P(OCH_2)_3CEt\}]$, *mer-trans*-$[MnH(CO)_3\{P(OCH_2)_3CEt\}_2]$, and *mer-trans*- and *mer-cis*-$[MnH(CO)_2\{P(OCH_2)_3CEt\}_3]$.

(*b*) *From* $[MnH(CO)_5]$ *in the absence of solvent.* Pentacarbonylhydridomanganese (5.8 g, 29.8 mmol) was distilled into an evacuated tube containing $P(OCH_2)_3CEt$ (3.22 g, 20 mmol), and the mixture was maintained at 0 °C for 4 h with periodic removal of the carbon monoxide evolved. The excess of $[MnH(CO)_5]$ was then removed under vacuum to give *cis*-$[MnH(CO)_4\{P(OCH_2)_3CEt\}]$ (4.4 g, 15 mmol, 75%).

(*c*) *From* $Na[Mn(CO)_4\{P(OCH_2)_3CEt\}]$. A solution of bis-[tetracarbonyl(trimethylolpropane phosphite)manganese] (1.4 g, 2.1 mmol) in freshly distilled sodium-dried tetrahydrofuran (60 cm^3) was added to 0.9% sodium amalgam (55 cm^3) and the mixture was stirred for 2 h before removal of the amalgam. Most of the solvent was removed from the residual solution and addition of 20% phosphoric acid (70 cm^3) in acetone (20 cm^3) caused precipitation of yellow-white crystals of *cis*-$[MnH(CO)_4\{P(OCH_2)_3CEt\}]$ (1.3 g, 3.9 mmol, 93%), which were recrystallised from acetone.

mer-trans-$[MnH(CO)_3\{P(OCH_2)_3CEt\}_2]$.—(*a*) *From* $[MnH(CO)_5]$. Addition of $[MnH(CO)_5]$ (4.6 g, 23.5 mmol) over 1.75 h to a stirred solution of $P(OCH_2)_3CEt$ (5.9 g, 36.4 mmol) in *p*-xylene (100 cm^3) at 100 °C, followed by further heating at the same temperature for 3 h, gave *mer-trans*-$[MnH(CO)_3\{P(OCH_2)_3CEt\}_2]$ (5.5 g, 11.8 mmol, 65%) as a white solid which precipitated on allowing the solution to cool. The product was recrystallised from benzene–light petroleum, b.p. 40—60 °C (3 : 1).

(*b*) *From cis*-[MnH(CO)$_4${P(OCH$_2$)$_3$CEt}] *in a solvent.* A slow stream of carbon monoxide was bubbled through a solution of *cis*-[MnH(CO)$_4${P(OCH$_2$)$_3$CEt}] (0.3 g, 0.9 mmol) and P(OCH$_2$)$_3$CEt (0.2 g, 1.2 mmol) in dioxan (15 cm^3) for 12 h at 10 °C. After this time addition of light petroleum (b.p. 40—60 °C) caused the precipitation of *mer-trans*-[MnH(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$] (0.33 g, 0.7 mmol, 80%).

(*c*) *From cis*-[MnH(CO)$_4${P(OCH$_2$)$_3$CEt}] *in the absence of a solvent.* An intimately ground mixture of *cis*-[MnH(CO)$_4$-{P(OCH$_2$)$_3$CEt}] (0.33 g, 1.0 mmol) and P(OCH$_2$)$_3$CEt (0.25 g, 1.5 mmol) heated at 90 °C for 14 h in a tube sealed under vacuum gave *mer-trans*-[MnH(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$] (0.38 g, 0.85 mmol, 85%) after removal of the excess of phosphite ligand by vacuum sublimation at 50 °C.

(*d*) *By reduction of fac*-[MnBr(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$]. The complex *fac*-[MnBr(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$] (0.4 g, 0.8 mmol, 24%) [ν(CO) at 2 070s, 2 015s, and 1 960s cm^{-1} (CH$_2$Cl$_2$ solution)] was obtained together with *mer-trans*-[MnBr(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$] [ν(CO) at 2 100w, 2 015s, and 1 960s cm^{-1} (CH$_2$Cl$_2$ solution)] by the addition of a solution of P(OCH$_2$)$_3$CEt (2.0 g, 12.5 mmol) in chloroform (10 cm^3) over 10 min to a solution of [MnBr(CO)$_5$] (1.0 g, 3.6 mmol) in the same solvent, and stirring the mixture for another 40 min. The products were precipitated by addition of light petroleum and separated by chromatography (Florisil) using light petroleum (b.p. 60—80 °C)—CH$_2$Cl$_2$ (4 : 1) as eluant.

Lithium aluminium hydride (*ca.* 1.0 g) was added over a period of 1 h to a stirred tetrahydrofuran solution of pure *fac*-[MnBr(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$] (0.2 g, 0.4 mmol) at room temperature, and stirring was continued for 1.5 h to give *mer-trans*-[MnH(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$] (0.08 g, 0.18 mmol, 45%).

mer-trans-[MnH(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$].—The reaction between [MnH(CO)$_4${P(OCH$_2$)$_3$CEt}] (1.1 g, 3.3 mmol) and P(OCH$_2$)$_3$CEt (2.0 g, 4.7 mmol) in dioxan (50 cm^3) at 20 °C for 24 h gave *mer-trans*-[MnH(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$] (1.0 g, 1.8 mmol, 54%) as a pale yellow solid purified by chromatography.

mer-trans- and mer-cis-[MnH(CO)$_2${P(OCH$_2$)$_3$CEt}$_3$].—An intimately ground mixture of *mer-trans*-[MnH(CO)$_3${P-(OCH$_2$)$_3$CEt}$_2$] (0.4 g, 0.86 mmol) and P(OCH$_2$)$_3$CEt (0.15 g, 0.93 mmol) heated at 115 °C for 15 h in a tube sealed under vacuum gave *mer-trans*-[MnH(CO)$_2${P(OCH$_2$)$_3$CEt}$_3$] (0.4 g, 0.67 mmol, 78%) after removal of the excess of phosphite ligand by sublimation at 50 °C (1 mmHg).* Recrystallisation from benzene–light petroleum (b.p. 30—40 °C) gave a quantitative conversion into *mer-cis*-[MnH(CO)$_2${P(OCH$_2$)$_3$-CEt}$_3$].

cis-[MnD(CO)$_4${P(OCH$_2$)$_3$CEt}].—A solution of Na[Mn-(CO)$_4${P(OCH$_2$)$_3$CEt}] in dry tetrahydrofuran (100 cm^3) was prepared from [Mn$_2$(CO)$_8${P(OCH$_2$)$_3$CEt}$_2$] (2.29, 3.3 mmol), and the solvent was then removed under vacuum to leave the sodium salt. This was dried by heating at 50 °C for 6 h under vacuum, followed by addition of DCl (30 cm^3, 10% solution in D$_2$O), which gave *cis*-[MnD(CO)$_4${P(OCH$_2$)$_3$-CEt}] (1.8 g, 5.5 mmol, 82%) as a pale yellow solid.

mer-trans-[MnD(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$].—An intimately ground mixture of *cis*-[MnD(CO)$_4${P(OCH$_2$)$_3$CEt}] (0.33 g, 1.0 mmol) and P(OCH$_2$)$_3$CEt (0.2 g, 1.2 mmol) heated at 90 °C for 14 h gave *mer-trans*-[MnD(CO)$_3${P(OCH$_2$)$_3$CEt}$_2$] (0.4 g, 0.86 mmol, 86%) after vacuum sublimation at 50 °C to remove the excess of phosphite.

mer-trans-[MnD(CO)$_2${P(OCH$_2$)$_3$CEt}$_3$].—Using a similar procedure to that described above, *mer-trans*-[MnD(CO)$_2$-{P(OCH$_2$)$_3$CEt}$_2$] (0.1 g, 0.21 mmol) and P(OCH$_2$)$_3$CEt (0.1 g, 0.6 mmol) heated at 105 °C for 50 h gave *mer-trans*-[MnD(CO)$_2${P(OCH$_2$)$_3$CEt}$_3$] (0.12 g, 0.17 mmol, 80%).

cis-[MnCl(CO)$_4${P(OCH$_2$)$_3$CEt}].—When a solution of *cis*-[MnH(CO)$_4${P(OCH$_2$)$_3$CEt}] (0.5 g, 1.5 mmol) in CCl$_4$ (25 cm^3) was heated for 16 h at 45 °C, followed by removal of the bulk of the solvent, *cis*-[MnCl(CO)$_4${P(OCH$_2$)$_3$CEt}] (0.4 g, 1.1 mmol, 70%) was precipitated as a pale yellow solid (Found: C, 32.3; H, 3.6. C$_{10}$H$_{11}$ClMnO$_7$P requires C, 32.9; H, 3.0%) with ν(CO) bands in the i.r. spectrum at 2 110w, 2 045m, 2 030s, and 1 977m–s cm^{-1}.

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

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