# Metal Carbonyl Chemistry. Part VII.[1] The Reaction of Ligands with Phenylpentacarbonylmanganese

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The preparation of phenyl- and benzoyl-manganese carbonyl complexes from the reactions of the ligands 1-ethyl-4-phospha-3,5,8-trioxabicyclo[2,2,2]octane, $P(OCH_2)_3CEt$, triphenylphosphine, or triphenyl phosphite with phenylpentacarbonylmanganese are described. The phosphite ligands lead to the formation of mono-, di-, and tri-substituted compounds of the type $PhCOMn(CO)_4L$, $PhMn(CO)_4L$, $PhCOMn(CO)_3L_2$, $PhMn(CO)_3L_2$, [where $L = P(OPh)_3$ or $P(OCH_2)_3CEt$], and $PhCOMn(CO)_2[P(OCH_2)_3CEt]_3$ depending on the reaction conditions employed. The reaction with triphenylphosphine gives cis-$PhMn(CO)_4PPh_3$, although some evidence was obtained for the intermediate formation of the unstable compound $PhCOMn(CO)_4PPh_3$. The stereochemistry of these compounds is discussed on the basis of their dipole moments, and infrared and ^1H n.m.r. spectroscopic measurements.

PREVIOUS work in this department [1,2] has shown that phenylpentacarbonylmanganese reacts with the ligands MPh_3 (where M = P, As, or Sb) in methylene chloride at room temperature to form cis-monosubstituted phenyl complexes. Alkyl or aryl phosphites under similar conditions replace two carbon monoxides in phenylpentacarbonylmanganese to give the $trans$-disubstituted phenyl or benzoyl complexes, $PhMn(CO)_3L_2$ or $PhCOMn(CO)_3L_2$ [L = $(PhO)_3P$ or $(PhO)_2PMe$] and phenyl complex $trans$-$PhMn(CO)_3[(MeO)_3P]_2$. It was tentatively suggested that these products arose by the intermediate formation of unstable mono- and di-substituted benzoyl complexes.

$$PhMn(CO)_5 \xrightarrow{L} PhCOMn(CO)_4L \xrightarrow{-CO} PhMn(CO)_4L$$
$$\xrightarrow{L} PhCOMn(CO)_3L_2 \xrightarrow{-CO} PhMn(CO)_3L_2$$
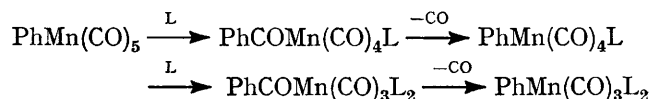
The reaction of phenylpentacarbonylmanganese with the bicyclophosphite ester, $P(OCH_2)_3CEt$, has now been investigated in an attempt to elucidate further the mechanisms of these reactions.

Reaction of Phenylpentacarbonylmanganese with 1-Ethyl-4-phospha-3,5,8-trioxabicyclo[2,2,2]octane.— The reaction of phenylpentacarbonylmanganese with an excess of the ligand $P(OCH_2)_3CEt$ in methylene chloride

at room temperature for 10 days gave 1 mol. of carbon monoxide evolved and the disubstituted benzoyl compound, cis $PhCOMn(CO)_3[P(OCH_2)_3CEt]_2$ (II) in 69% yield. This compound has been shown to arise by the intermediate formation of cis-$PhCOMn(CO)_4[P(OCH_2)_3CEt]$ (I) (Scheme 1), since under similar conditions equimolar quantities of the reactants gave both (I) (14% yield) and (II) (12% yield) after 7 days.

The reaction of benzoylpentacarbonylmanganese with an excess of the ligand at room temperature for 22 hours in methylene chloride also gave (II) (40% yield) in addition to (I) (60% yield). It has also been shown by infrared spectroscopy that (II) is formed quantitatively in the reaction of (I) with an excess of ligand at room temperature in chloroform for 2 days.

No evidence was obtained in any of these reactions for the intermediate formation of the compound $trans$-$PhCOMn(CO)_4P(OCH_2)_3CEt$. This compound was therefore prepared (8% yield) together with the cis-isomer (72% yield) from the reaction of benzoyl chloride with the salt $NaMn(CO)_4P(OCH_2)_3CEt$ in tetrahydrofuran at room temperature; both isomers are stable compounds which show no tendency to rearrange at room temperature in solution.

Compound (I) decarbonylates smoothly to give

[1] Part VI, W. D. Bannister, B. L. Booth, M. Green, and R. N. Haszeldine, *J. Chem. Soc.* (*A*), 1968, 698.

[2] W. D. Bannister, M. Green, and R. N. Haszeldine, *Chem. Comm.*, 1965, 54.

PhMn(CO)$_4$P(OCH$_2$)$_3$CEt (V) in 61% yield (110° in the absence of solvent) or in 78% yield (80° for 2 hr. in chloroform; a 3% yield of phenylpentacarbonyl-

TABLE 1

Action of heat on
cis-PhCOMn(CO)$_3$[P(OCH$_2$)$_3$CEt]$_2$

Reactant (mmoles)	Solvent	Temp. (°c)	Time (hr.)	Yield of (III) (%)	Yield of (IV) (%)	Yield of (V) (%)
1·31	Chloroform	60	3	—	—	45
2·52	,,	60	18·5	12	42	31
1·47	,,	80	23	82	—	—
1·95	Toluene	110	20	84	—	—
5·4	None	130	0·5	72	—	—

manganese is also formed). Dipole moment measurements and ^{1}H n.m.r. spectroscopy indicate that the decarbonylation product is probably a mixture of cis- and trans-isomers.

When the cis-compound (II) is heated at 130° under nitrogen, 1 mol. of carbon monoxide is evolved to give

SCHEME 1   Reaction of phenylpentacarbonylmanganese with P(OCH$_2$)$_3$CEt(L)
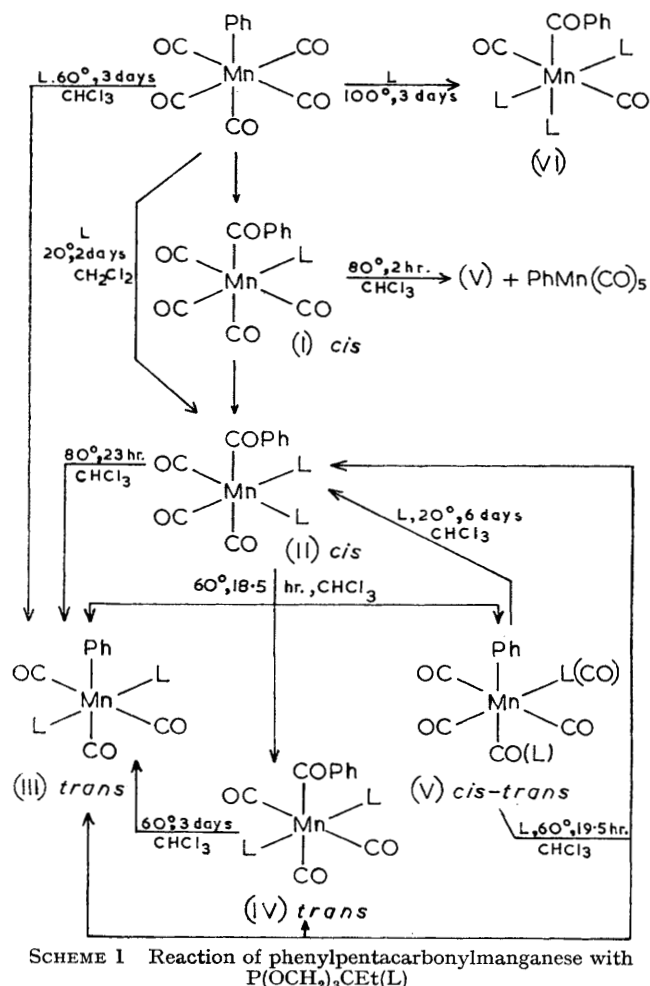
trans-PhMn(CO)$_3$[P(OCH$_2$)$_3$CEt]$_2$ (III) in 72% yield. The same compound is obtained (82% yield) when (II) is heated in chloroform or other solvents (Table 1; Scheme 1) and also when phenylpentacarbonylmanga-

nese reacts with an excess of the ligand in refluxing chloroform (72% yield).

There is little doubt that the cis–trans rearrangement reaction occurs prior to the decarbonylation reaction, since reaction at a lower temperature for a shorter time reduces the yield of (III), and the main reaction products are trans-PhCOMn(CO)$_3$[P(OCH$_2$)$_3$CEt]$_2$ (IV) and the previously mentioned compound (V) (Scheme 1); a small amount of free ligand can also be isolated from this reaction. Compound (IV) decarbonylates smoothly (60° for 3 days in chloroform) to give (III) in 97% yield; attempts to carbonylate compound (III) with carbon monoxide (40 atm.) at room temperature (3 days) were unsuccessful. When compound (II) was heated at 60° for 24 hr. in chloroform with the solution monitored by infrared spectroscopy the initial product was compound (V) which then underwent further reaction to give the compounds (III) and (IV). Table 1 also shows that when reaction is terminated after only 3 hr. only (V) is obtained (45% yield). The formation of compound (V) from (II) is reversible since reaction with an excess of the ligand in chloroform at room temperature converts (V) into (II) in 59% yield. If the reaction of (V) with the ligand (ratio 1 : 1) is carried out at 60° in the same solvent the products are compounds (IV) (54% yield), (II) (24%), and (III) (17%). Phenylpentacarbonylmanganese heated with an excess of the ligand in the absence of a solvent at 100° gives the compound trans-PhCOMn(CO)$_2$[P(OCH$_2$)$_3$CEt]$_3$ (VI) (Scheme 1) (16% yield), together with the compounds (III) (31%) and (IV) (42%).

In view of the complexity of the reaction of phenylpentacarbonylmanganese with the ligand P(OCH$_2$)$_3$CEt, and the close analogy between the reaction with this ligand and other phosphine and phosphite ligands, the reactions with the ligands Ph$_3$P and (PhO)$_3$P were reinvestigated.

Reaction of Phenylpentacarbonylmanganese with Triphenylphosphine.—The reaction between phenylpentacarbonylmanganese and triphenylphosphine at room temperature for 4·5 hr. in tetrahydrofuran gave only a fraction of the theoretical amount of carbon monoxide required for the loss of one CO molecule. The product was an unstable solid, presumably PhCOMn(CO)$_4$PPh$_3$, which showed a band at 1724 cm.$^{-1}$ in its i.r. spectrum attributed to acyl carbonyl. Attempts to purify the compound chromatographically or to recrystallise it led to vigorous gas evolution, and the isolated product was the previously described [1,2] compound, cis-PhMn-(CO)$_4$PPh$_3$.

Reaction of Phenylpentacarbonylmanganese with Triphenyl Phosphite.—Under similar conditions to those used with triphenylphosphine the ligand (PhO)$_3$P gave only the compound PhCOMn(CO)$_4$P(OPh)$_3$ (VII) (Scheme c; 40% yield), shown by infrared spectroscopy to be a mixture of cis- and trans-isomers. Decarbonylation of (VII) at 100° gave cis-PhMn(CO)$_4$P(OPh)$_3$ (VIII) (Scheme 2; 34% yield). Reaction of phenylpentacarbonylmanganese with an excess of triphenyl phos-

II

phite in tetrahydrofuran at room temperature for 3 days gave the compound *trans*-PhCOMn(CO)₃[P(OPh)₃]₂ (IX) (Scheme 2; 33% yield) in addition to compound (VII) (59% yield). The yield of compound (IX) was in-
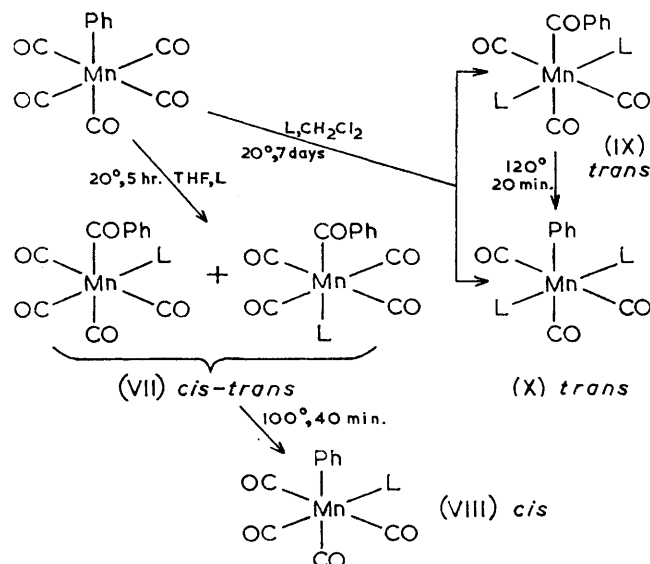
SCHEME 2 Reaction of phenylpentacarbonylmanganese with (PhO)₃P (L)

creased to 50% by carrying out the reaction in methylene chloride for 7 days at room temperature. The compound *trans*-PhMn(CO)₃[P(OPh)₃]₂ (X) (Scheme 2) previously reported [2] as the major product in this reaction

Infrared Spectra.—The monosubstituted complexes PhMn(CO)₄L [L = P(OCH₂)₃CEt, (PhO)₃P, or Ph₃P] and PhCOMn(CO)₄P(OCH₂)₃CEt show four bands ($3A' + A''$) in the metal carbonyl region (Table 2), consistent with these compounds having C_s symmetry with the organic group and substituting ligand in mutually *cis*-positions. This pattern has been previously observed in other compounds of the type *cis*-XMn(CO)₄L (X = CH₃,[3,4] Cl, Br, I,[3] or H;[5] L = Ph₃P. X = Ph;[1,2] L = Ph₃As[1,2] or Ph₃Sb[1,2]). The benzoyl complex also shows a strong band at 1597 cm.⁻¹ assigned to an acyl group and absent from the spectra of the phenyl complexes. The n.m.r. spectrum of the compound PhMn(CO)₄-P(OCH₂)₃CEt (see later) suggests the presence of more than one isomer, but this is not apparent from its i.r. spectrum.

The compound *trans*-PhCOMn(CO)₄P(OCH₂)₃CEt shows, in addition to a strong absorption at 1600 cm.⁻¹ (acyl CO group), three terminal carbonyl stretching absorptions instead of the two bands ($A_1 + E$) expected for C_{4v} symmetry. N.m.r. spectroscopic studies, however, show the presence of about 10% of the *cis*-isomer which could explain the weak absorption at 2087 cm.⁻¹; alternatively this band may be caused by distortion of the molecule from true C_{4v} symmetry with appearance of the B_1 mode, normally inactive in the i.r. spectrum. Similar spectra have been observed with other *trans*-monosubstituted complexes,[4,6] but these also probably contained some *cis*-isomer.[7] The moderate intensity absorption at 2030 cm.⁻¹ can be assigned to the A_1 mode, and the strong absorption at 1984 cm.⁻¹ to the

TABLE 2

Infrared absorptions of manganese complexes

Compound	M.p.	Carbonyl stretching frequencies (cm.⁻¹) [a]				
L = P(OCH₂)₃CEt						
cis-PhCOMn(CO)₄L	105 [e]	2087m	2010s	1988s	1975s	1597s
trans-PhCOMn(CO)₄L	102 [e]	2087w	2030m–s	1984s		1600s [b]
cis-trans-PhMn(CO)₄L	107—108	2079m	2004s	1987s	1965s	
cis-PhCOMn(CO)₃L₂	107 [e]	2031s	1961s	1947s		1597s
trans-PhCOMn(CO)₃L₂	197 [e]	2058w	1975s	1954s,sh		1592s
trans-PhMn(CO)₃L₂	197 [e]	2044w	1960s	1941s,sh		
trans-PhCOMn(CO)₂L₃	132	2024w	1933s			1553s
L' = (PhO)₃P						
cis-trans-PhCOMn(CO)₄L'	72—74 [e]	2077m	2068w	2077s	1980s	1968s [b,c,d] 1560s
cis-PhCOMn(CO)₄L'	85—86	2078m	2022s	2010s	1989s [b,c]	
trans-PhCOMn(CO)₄L'₂	135—136 [e]	2044m	1965s	1942s [b]		1560s
trans-PhMn(CO)₃L'₂	137—138 [f]	2043m	1960s	1945s [b,d]		

[a] Solutions in CH₂Cl₂ measured on a Perkin-Elmer model 21 instrument with CaF₂ optics, scale expanded by 4 in the 4—6 region, unless otherwise stated. [b] Perkin-Elmer 257 grating instrument. [c] Solutions in n-hexane. [d] Lit.,[1,2] 2016m, 1968s, 1934s. [e] With decomposition; decarbonylation to the phenylmanganese compound may have occurred before melting. [f] Lit.,[1,2] 146·5—147·5°.

was obtained in only 10% yield. Compound (IX) loses 1 mol. of carbon monoxide at 120° to give (X) quantitatively.

The evidence for the structural assignments of the compounds prepared in this work is now discussed.

E mode; no splitting of the E mode was observed, but the spectrum was recorded in methylene chloride owing to its insolubility in hydrocarbon solvents, and this would lead to band broadening and loss of resolution.

The compound PhCOMn(CO)₄P(OPh)₃ shows five terminal carbonyl bands, indicating that it is a mixture

[3] W. Hieber, G. Faulhaber, and F. Theubert, *Z. anorg. Chem.*, 1962, **314**, 125.
[4] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1964, **86**, 5043.
[5] B. L. Booth and R. N. Haszeldine, *J. Chem. Soc.* (*A*), 1966, 157.

[6] R. J. Mawby, D. Morris, E. M. Thorsteinson, and F. Basolo, *Inorg. Chem.*, 1966, **5**, 27.
[7] K. Noack, M. Ruch, and F. Calderazzo, *Inorg. Chem.*, 1968, **7**, 345.

of isomers. The compound $CH_3COMn(CO)_4PPh_3$ has also been shown to exist as an equilibrium mixture of isomers in solution, in which the *cis*-isomer predominates.[7] In addition the spectrum shows a strong band at 1560 cm.$^{-1}$ from the acyl group which is partially masked by a strong band at 1590 cm.$^{-1}$ from the ligand; the band at 1560 cm.$^{-1}$ is not present in the spectrum of *cis*-PhMn-$(CO)_4P(OPh)_3$.

The disubstituted complex (II), $PhCOMn(CO)_3$-$[P(OCH_2)_3CEt]_2$ shows three strong bands $(2A' + A'')$ of approximately equal intensity in the metal carbonyl region (Table 2) together with a strong acyl band at 1597 cm.$^{-1}$. This is consistent with a stereochemistry (C_s symmetry) in which the two ligand molecules are *cis* to each other and *cis* to the benzoyl group. Similar spectra have previously been observed for the complexes *cis*-XMn(CO)$_3$L$_2$ [X = H[5] or Br;[8] L = (PhO)$_3$P)] and *cis*-HMn(CO)$_3$(Ph$_2$P·CH$_2$)$_2$.[5]

The disubstituted compounds PhCOMn(CO)$_3$L$_2$ [L = P(OCH$_2$)$_3$CEt (IV) or (PhO)$_3$P] and PhMn(CO)$_3$L$_2$ [L = P(OCH$_2$)$_3$CEt or P(OPh)$_3$] also show three bands in the metal carbonyl region (Table 2), but the band at highest frequency is of weak intensity. Infrared spectroscopy alone does not enable a distinction to be made between a structure in which the ligands are *trans* to each other and *cis* to the organic ligand (C_{2v} symmetry), or the alternative structure in which one ligand is *cis* and the other *trans* to the organic ligand (C_s symmetry). However, additional evidence for C_{2v} symmetry in the case of compounds containing the ligand P(OCH$_2$)$_3$CEt is unambiguously provided by a study of their n.m.r. spectra (see later), but the stereochemistry of complexes containing the ligand P(OPh)$_3$ cannot be confirmed by this technique. By analogy with the established *trans*-configuration of the disubstituted phenyl complexes obtained from the reaction of phenylpentacarbonylmanganese with the similar phosphite ligands P(OCH$_2$)$_3$CEt and (PhO)$_2$PMe,[1,2] it could be assumed that the compound PhMn(CO)$_3$[P(OPh)$_3$]$_2$, and hence the corresponding benzoyl compound, also have C_{2v} symmetry, especially since the compound *cis*-PhMn-(CO)$_3$(Ph$_2$P·CH$_2$)$_2$, previously shown[1,2] to have the alternative C_s symmetry, shows only two strong carbonyl bands in its infrared spectrum even under high resolution, in contrast to the three bands observed for the C_{2v} symmetry compounds. The i.r. spectrum of the compound *trans*-PhCOMn(CO)$_3$[(PhO)$_3$P]$_2$ shows an acyl band (1560 cm.$^{-1}$) partially masked by a strong band from the ligand; this band at 1560 cm.$^{-1}$ is absent from the spectrum of *trans*-PhMn(CO)$_3$[(PhO)$_3$P]$_2$.

The trisubstituted compound, PhCOMn(CO)$_2$-$[P(OCH_2)_3CEt]_3$ shows two bands in the carbonyl region (Table 2) the one at highest frequency being of weak intensity. The spectrum also shows a strong acyl band which is shifted to slightly lower frequency com-

pared with the mono- and di-substituted benzoyl complexes. There are three possible structures for this compound. Structure (A) might be expected to show two strong bands of approximately equal intensity in
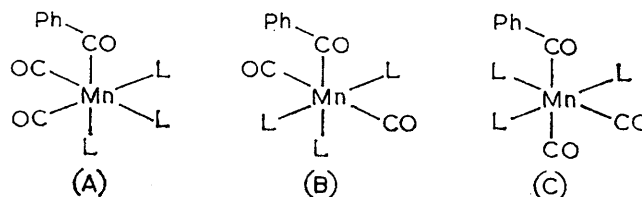
the carbonyl region. Structure (C) might also be expected to have two strong carbonyl bands, although prediction of the ratio of their intensities is less certain. Structure (B) (C_{2v} symmetry), however, should have only one strong band (B_1) in the carbonyl region as observed for the isolated compound. The additional weak band also observed in the spectrum may arise by the distortion of the molecule from ideal C_{2v} symmetry.

Nuclear Magnetic Resonance Spectra.—The ^{1}H n.m.r. spectra of the complexes formed from the ligands Ph$_3$P and (PhO)$_3$P exhibit only one broad, complex band at τ 2—3 caused by overlap of the proton resonances of the phenyl groups on the phosphine or phosphite ligand with the phenyl group attached directly to the manganese atom or acyl CO group. These spectra give no information on the stereochemistry of the complexes and will not be discussed further. The n.m.r. spectrum of the ligand P(OCH$_2$)$_3$CEt in the free state consists of a triplet and a quartet near τ 9 (ethyl group), and a symmetrical doublet ($|J|_{POCH}$ 1·9 c./sec.) for the bridging methylene protons coupled with phosphorus. The co-ordinated ligand in the compounds *cis*-PhCOMn(CO)$_4$P(OCH$_2$)$_3$CEt and *trans*-PhCOMn(CO)$_4$P(OCH$_2$)$_3$CEt shows a similar n.m.r. pattern, but the bridging methylene protons absorb at a slightly lower field strength and there is a considerable increase in the coupling constant $|J|_{POCH}$. Similar effects have previously been observed in the spectra of other monosubstituted carbonyl derivatives containing related phosphorus ligands.[9–11] The compound PhMn(CO)$_4$P(OCH$_2$)$_3$CEt, which would also be expected to show only a doublet for the bridging methylene protons of the ligand, shows a 1 : 1 : 1 : 1 quartet in this region, and this indicates the presence of two isomers in approximately equal amounts giving rise to overlapping doublets.

It has been shown[10,11] that the pattern of the bridging methylene proton resonances of bicyclo-phosphite ligands can, in the case of disubstituted complexes, give valuable information on their stereochemistry. The compounds *trans*-PhCOMn(CO)$_3$[P(OCH$_2$)$_3$CEt]$_2$ (IV) and *trans*-PhMn(CO)$_3$[P(OCH$_2$)$_3$CEt]$_2$ show a well defined 1 : 2 : 1 triplet in this region instead of the doublet observed with the monosubstituted compounds caused by strong

[8] R. J. Angelici, F. Basolo, and A. J. Poë, *J. Amer. Chem. Soc.*, 1963, **85**, 2215.

[9] J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 1963, 279; *J. Chem. Soc. (A)*, 1966, 770.

[10] J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *Inorg. Chem.*, 1965, **4**, 228.

[11] J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *Inorg. Chem.*, 1966, **5**, 639.

phosphorus–phosphorus coupling across the *trans*-position, which has been attributed to a strong *trans*-effect between the two ligands.[9] Similar strong coupling of *trans*-phosphorus ligands in octahedral complexes has previously been observed for the compounds $PhMn(CO)_3$-$[(PhO)_2PMe]$ [1,2] and $M(CO)_4L_2$ [M = Cr, Mo, W; L = $P(OCH_2)_3CMe$,[10] 2,8,9-trioxaphospha-adamantane, $[P(OCH)_3(CH_2)_3]$,[11] or $P(NMe_2)_3$ [12]]. The alternative
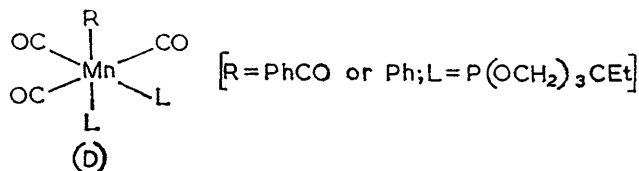
structure (D) for these complexes can be discounted, as in compounds of this type the ligands are in different environments and might be expected to give a more

complexes of the same ligands exhibit strong coupling. Strong P–P coupling has also been observed [13] in the *cis*-disubstituted rhodium complexes π-C_5H_5Rh-$[P(OCH_3)_3]_2$ and π-$C_5H_5Rh[P(OCH_2)_3CMe]_2$.

The complex (II), *cis*-$PhCOMn(CO)_3[P(OCH_2)_3CEt]_2$, which by analogy with the square planar complexes might have been expected to give no P–P coupling and exhibit a doublet for the bridging methylene resonances, showed a poorly resolved 1 : 2 : 1 triplet in this region (Table 3), even though resolution of the ethyl protons of the ligand was good, and the spectrum was recorded at 0°. This suggests that weak coupling ($|J|_{P–P}$ calc. < 10 c./sec.) occurs between the *cis*-phosphorus atoms in this complex and results in a reduction in intensity of the central band of the triplet, and that this coupling is much weaker than that observed for the analogous *trans* complex.* The spectrum of the trisubstituted complex shows only a broad band in the bridging

TABLE 3

Nuclear magnetic resonance data for some manganese complexes

Compound	Chemical shift (τ)		Coupling constant (c./sec.)	
	[1]H phenyl	[1]H ligand [a]	$|J|_{POCH}$	$|J|_{P-P}$ [b]
L = $P(OCH_2)_3CEt$		6·02 (doublet)	1·9	
$PhMn(CO)_5$	2·60(2)			
	2·90(3)			
$PhCOMn(CO)_5$	2·55			
trans-$PhCOMn(CO)_4L$	2·62	5·78 (doublet)	4·5	
cis-$PhCOMn(CO)_4L$	2·64	5·69 (doublet)	5·0	
cis-trans-$PhMn(CO)_4L$	2·42(2)	5·87 (1 : 1 : 1 : 1) (quartet)	4·5,[d] 4·7 [e]	
	3·02(3)			
cis-$PhCOMn(CO)_3L_2$ [f]	2·68	5·75 (triplet)	~5·0 [c]	5 ± 2
trans-$PhCOMn(CO)_3L_2$	2·88	5·78 (triplet)	4·6 [c]	70 ± 20
trans-$PhMn(CO)_3L_2$	2·45(2)	5·84 (triplet)	4·7 [c]	110 ± 40
	3·15(3)			
trans-$PhCOMn(CO)_2L_3$	2·78	5·84 (broad singlet)		

[a] Only the bridging methylene resonances are given here. All compounds containing L showed a complex multiplet at τ ca. 9 in addition. [b] Calculated from the expression $Q = [|J|_{AX}^2 + |J|_{AA'}^2]^{\frac{1}{2}}$ derived by Verkade *et al.*[10,11] [c] $|J|_{POCH}$ in this case refers to the separation of the two outside absorptions of the triplet. [d] $|J|_{POCH}$ refers to the separation between the 3rd and 4th absorption from the reference. [e] $|J|_{POCH}$ refers to the separation between the 1st and 3rd absorption from the reference. [f] Spectrum recorded at 0° with an A.E.I. R.S.2 instrument at 60 Mc./sec.; methylene chloride solution using tetramethylsilane as internal reference.

complex pattern in the methylene proton region than the sharp 1 : 2 : 1 triplet observed.

Crude estimates of the values of $|J|_{P–P}$ have been made by the treatment previously described [10,11] for a similar ligand, for the *trans*-disubstituted phenyl and benzoyl complexes prepared in this work, and give values of the order of 70—110 c./sec. (Table 3) in good agreement with the values obtained for other *trans*-disubstituted compounds.[11]

Phosphorus–phosphorus coupling in *cis*-disubstituted transition metal complexes is dependent upon the geometry of the complex. Disubstituted square planar platinum and palladium complexes of the ligand PMe_2Ph exhibit no P–P coupling when the ligands are in the *cis*-position, but there is strong coupling between *trans*-ligands.[9] No coupling occurs in disubstituted tetrahedral nickel complexes of the ligands $P(OCH_2)_3CMe$ [10,11] and $P(OCH)_3(CH_2)_3$,[11] but tri- and tetra-substituted

methylene region, which is not inconsistent with the assigned structure.

The [1]H n.m.r. spectra of the benzoyl complexes prepared in this work all show only a single band (τ 2·6—2·9) for the aromatic protons, whereas those of the phenyl complexes appear as two distinct bands (τ 2·4—2·6 and 2·9—3·2) with an intensity ratio of 2 : 3 (Table 3). Similar splitting of the aromatic protons of phenyl-pentacarbonylmanganese, recently observed,[14] appears to be diagnostic for a phenyl group attached to a manganese carbonyl residue. A possible explanation of this may lie in the diamagnetic anisotropy of the metal carbonyl groups; models show that the two *ortho*-protons of the phenyl group lie close to the centre of the radial carbonyl groups, and these protons might be expected to experience abnormal deshielding resulting in a shift to lower field. Similar deshielding by metal

[12] R. B. King, *Inorg. Chem.*, 1963, **2**, 936.
[13] H. G. Schuster-Woldan and F. Basolo, *J. Amer. Chem. Soc.*, 1966, **88**, 1657.
[14] K. Noack, V. Schaerer, and F. Calderazzo, *J. Organometallic Chem.*, 1967, **8**, 517.

* Similar phosphorus–phosphorus coupling of *cis*-phosphite ligands has recently been observed for the compounds *cis*-$MeCOMn(CO)_3[P(OCH_2)_3CMe]_2$ (P. K. Maples and C. S. Kraihanzel, *Chem. Comm.*, 1968, 922) and *cis*-$M(CO)_3[P(OCH_2)_3CR]_3$, where M = Cr, Mo, or W and R = Me, Et, or Pr[n] (W. E. Stanclift and D. G. Hendricker, *Inorg. Chem.*, 1968, **7**, 1242).

carbonyl groups has been described for some tri(tertiary arsine) derivatives of metal carbonyls.[15] The *ortho*-protons are further removed from the radial carbonyl groups in the benzoyl complexes, and this deshielding effect cannot arise.

Dipole Moments.—The dipole moments of the compounds PhCOMn(CO)$_3$[P(OCH$_2$)$_3$CEt]$_2$ (IV) and

TABLE 4

· Dipole moments of some manganese carbonyl complexes in benzene at 20°

Compound [a]	μ_D (Debye)
cis-PhCOMn(CO)$_4$L	5·8 [b]
cis-trans-PhMn(CO)$_4$L	4·0 [b]
cis-PhCOMn(CO)$_3$L$_2$	6·2 ± 0·1
trans-PhCOMn(CO)$_3$L$_2$	2·5 ± 0·1
trans-PhMn(CO)$_3$L$_2$	1·69 ± 0·03
trans-PhCOMn(CO)$_2$L$_3$	5·1 ± 0·3

[a] L = P(OCH$_2$)$_3$CEt. [b] Approximate values since association occurs in benzene.

PhMn(CO)$_3$[P(OCH$_2$)$_3$CEt]$_2$ (III) are both low (Table 4), and support their assignment as *trans*-structures. The much larger dipole observed for compound (II), PhCOMn-

cis-structure, and thus supports the n.m.r. spectroscopic evidence that this compound is a mixture of *cis*- and *trans*-isomers. The moment of the compound PhCOMn-(CO)$_2$[P(OCH$_2$)$_3$CEt]$_3$ supports the conclusion from its i.r. spectrum that this compound does not have structure (A) but fails to distinguish between the remaining two possible structures.

DISCUSSION

The results available for the ligands P(OCH$_2$)$_3$CEt and P(OPh)$_3$ are summarised in Scheme 3. The formation of *cis*-PhCOMn(CO)$_4$P(OCH$_2$)$_3$CEt as the initial product in the reaction of phenylpentacarbonylmanganese with P(OCH$_2$)$_3$CEt is considered to occur by a phenyl migration mechanism, by analogy with the existing evidence obtained from a study of similar reactions.[4,17,18] It is apparent that the bicyclo-phosphite ligand is much more effective at stabilising organic ligands than are other phosphite and phosphine ligands, since the compound *cis*-PhCOMn(CO)$_4$P(OCH$_2$)$_3$CEt shows no tendency either to decarbonylate or to rearrange in solution at room

	PhMn(CO)$_5$		
[(I) *cis*; L = P(OCH$_2$)$_3$CEt (VII) *cis* and *trans*; L = (PhO)$_3$P]	PhCOMn(CO)$_4$L	$\xrightarrow{-CO}$	PhMn(CO)$_4$L [(V) *cis* and *trans*; L = P(OCH$_2$)$_3$CEt (VIII) *cis*; L = (PhO)$_3$P]
[(II); L = P(OCH$_2$)$_3$CEt]	*cis*-PhCOMn(CO)$_3$L$_2$		
[(IV); L = P(OCH$_2$)$_3$CEt (IX); L = (PhO)$_3$P]	*trans*-PhCOMn(CO)$_3$L$_2$		
[(III); L = P(OCH$_2$)$_3$CEt (X); L = (PhO)$_3$P]	*trans*-PhMn(CO)$_3$L$_2$		
[(VI); L = P(OCH$_2$)$_3$CEt]	*trans*-PhCOMn(CO)$_2$L$_3$		
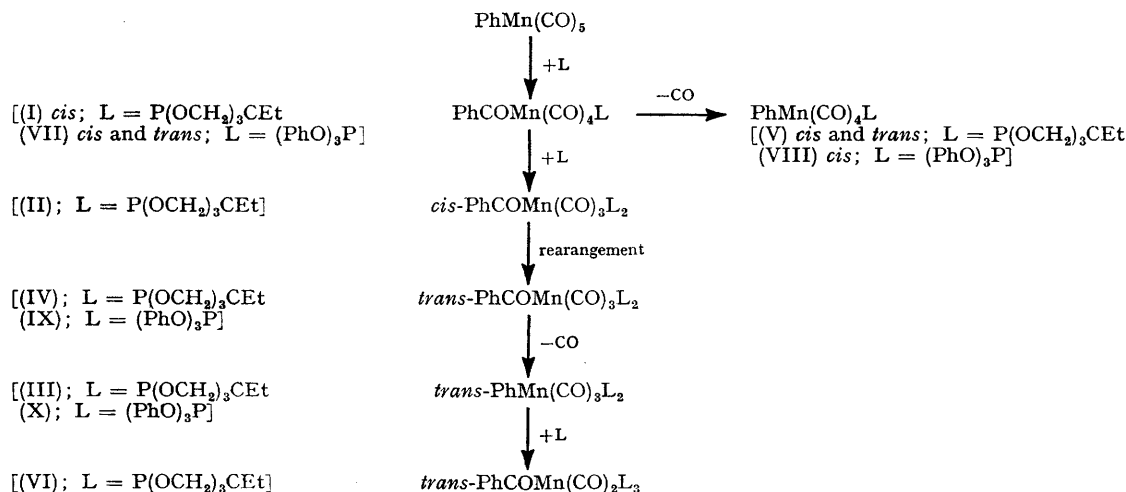
SCHEME 3

(CO)$_3$[P(OCH$_2$)$_3$CEt]$_2$, is in agreement with i.r. spectroscopic evidence, and supports a structure in which the two ligands are in a *cis*-configuration. The calculated moment for $\overset{+}{L}-\overset{\longrightarrow}{M}-CO$ in this molecule is *ca.* 4 D. Although difficulty was experienced in obtaining the dipole moment of the complex *cis*-PhCOMn(CO)$_4$P-(OCH$_2$)$_3$CEt, since association occurred in benzene solution, the value obtained supported the *cis*-configuration, based on the calculated value for the L–Mn–CO dipole and the figure reported[16] for benzoylpentacarbonyl-manganese [μ_DPhCOMn(CO)$_5$ 2·09 ± 0·04 D]. The observed dipole moment for the compound PhMn-(CO)$_4$P(OCH$_2$)$_3$CEt is less than the value expected for a

temperature. The analogous compound, *cis*-CH$_3$COMn-(CO)$_4$P(OCH$_2$)$_3$CEt, has also been recently shown to be stable under these conditions.[19] Although evidence has been obtained for the formation of a compound PhCOMn(CO)$_4$PPh$_3$ from the reaction of phenylpenta-carbonylmanganese and triphenylphosphine, it readily decomposes at room temperature to give the isolated compound *cis*-PhMn(CO)$_4$PPh$_3$. Similarly, it has been shown that the reaction of phenylpentacarbonyl-manganese with triphenyl phosphite gives a mixture of *cis*- and *trans*-PhCOMn(CO)$_4$P(OPh)$_3$, probably by rapid rearrangement of the initially formed *cis*-PhCOMn-(CO)$_4$P(OPh)$_3$ as previously observed for the compound CH$_3$COMn(CO)$_4$PPh$_3$.[7,20] This increased stability of

[15] R. S. Nyholm, M. R. Snow, and M. H. B. Stiddard, *J. Chem. Soc.*, 1965, 6564.
[16] W. Beck, W. Hieber, and H. Tengler, *Chem. Ber.*, 1961, **94**, 862.
[17] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1964, **87**, 5767.
[18] K. Noack and F. Calderazzo, *J. Organometallic Chem.*, 1967, **10**, 101.
[19] M. Green and D. C. Wood, *J. Amer. Chem. Soc.*, 1966, **88**, 4106.
[20] C. S. Kraihanzel and P. K. Maples, *J. Amer. Chem. Soc.*, 1965, **87**, 5267.

the complexes containing the ligand $P(OCH_2)_3CEt$ can be interpreted in terms of the better acceptor properties of the ligand, compared with phosphine ligands, and its small steric requirements.

The decarbonylation of the compound *cis*-PhCOMn-$(CO)_4P(OCH_2)_3CEt$ to give a mixture of *cis*- and *trans*-PhMn(CO)$_4$P(OCH$_2$)$_3$CEt contrasts with previous observations on the decarbonylation reactions of *cis*-CH$_3$COMn(CO)$_4$P(OCH$_2$)$_3$CEt [19] and *cis*- and *trans*-CH$_3$COMn(CO)$_4$PPh$_3$ [7,20] which are reported to give the *cis*-methyl complexes exclusively. Similarly, in this work, decarbonylation of *cis*- and *trans*-PhCOMn-(CO)$_4$P(OPh)$_3$ gave exclusively *cis*-PhMn(CO)$_4$P(OPh)$_3$. The formation of both the *cis*- and *trans*-isomers of PhMn(CO)$_4$P(OCH$_2$)$_3$CEt can readily be explained by migration of the phenyl group into the positions *cis* or
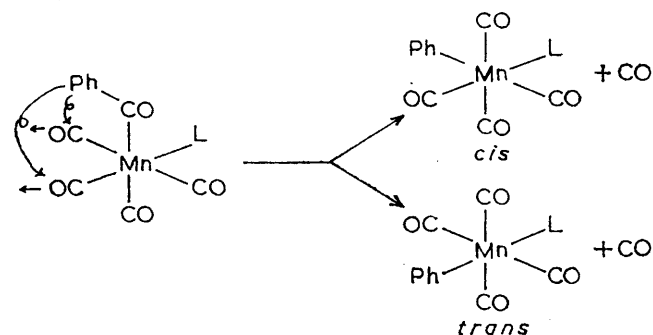
trans to the phosphite ligands, although the alternative explanation of acyl CO migration, which would require some initial isomerisation of the *cis*- to the *trans*-benzoyl complex, cannot be completely discounted.

It is interesting that in the decarbonylation reaction of *cis*-PhCOMn(CO)$_4$P(OCH$_2$)$_3$CEt a small amount of phenylpentacarbonylmanganese was also isolated, suggesting that there is a competing reaction whereby phenyl migration occurs with displacement of phosphite ligand rather than carbon monoxide. A similar displacement of triphenylphosphine on carbonylation of *cis*-PhMn(CO)$_4$PPh$_3$ has recently been reported.[1,2]

The formation of *cis*-PhCOMn(CO)$_3$[P(OCH$_2$)$_3$CEt]$_2$ on treatment of the *cis*-monosubstituted benzoyl complex with an excess of the ligand demonstrates the facile displacement of the carbon monoxide *cis* to the ligand, and the importance of the *trans*-effect in octahedral manganese complexes. The available experimental evidence for the mechanism of the conversion of *cis*-PhCOMn(CO)$_3$[P(OCH$_2$)$_3$CEt]$_2$ into *trans*-PhMn(CO)$_3$[P-(OCH$_2$)$_3$CEt]$_2$ is consistent with an initial reversible reaction of phenyl migration with the displacement of a phosphite ligand to form PhMn(CO)$_4$[P(OCH$_2$)$_3$CEt]. A comparison of this reaction with the corresponding decarbonylation reaction of *trans*-PhCOMn(CO)$_3$[P-(OCH$_2$)$_3$CEt]$_2$ clearly indicates that in complexes containing *trans*-CO ligand phenyl migration occurs with loss of carbon monoxide, but in compounds in which both

radial CO molecules are *trans* to the phosphite ligand, phenyl migration occurs with preferential loss of the phosphite ligand. The formation of *trans*-PhCOMn-(CO)$_3$[P(OCH$_2$)$_3$CEt]$_2$ in the rearrangement reaction is considered to arise by further attack by the displaced phosphite ligand on the compound PhMn(CO)$_4$P-(OCH$_2$)$_3$CEt; decarbonylation of *trans*-PhCOMn(CO)$_3$[P-(OCH$_2$)$_3$CEt]$_2$ has further been shown to give an almost quantitative yield of the compound *trans*-PhMn(CO)$_3$-[P(OCH$_2$)$_3$CEt]$_2$.

It is considered that this rearrangement reaction occurs in all the reactions of phenylpentacarbonyl-manganese with the phosphite ligands (PhO)$_3$P, (CH$_3$O)$_3$P, and (PhO)$_2$PMe studied in this work and previously.[1,2] Although these reactions have not been investigated in the same detail and the mechanism has not been rigorously established, the final isolated products were *trans*-disubstituted complexes; in the case of at least one of these ligands, namely (PhO)$_3$P, one of the intermediate compounds, *trans*-PhCOMn(CO)$_3$[(PhO)$_3$P]$_2$, has now been positively characterised.

The results of a kinetic study of some of these reactions will be discussed in a further publication.

EXPERIMENTAL

Infrared spectra were recorded on Perkin-Elmer models 21 or 257 spectrophotometers, and ^{1}H n.m.r. spectra were recorded on a Perkin-Elmer R.10 high-resolution spectrometer at 60 Mc./sec. using methylene chloride as solvent and tetramethylsilane as internal reference. Dipole moments were measured in benzene using a Wissenshaftlich–Technische Werkstätten instrument type DM01 operating at 2 Mc./sec. Refractive indices were determined with a Pulfrich refractometer. Molecular weight determinations were carried out using a Mechrolab vapour pressure osmometer.

Phenyl- and benzoyl-pentacarbonylmanganese were prepared from decacarbonyldimanganese by a method similar to that previously reported[16] for *p*-tolyl- and *p*-toluoyl-pentacarbonylmanganese. The phenyl compound, m.p. 51° (lit.,[21] 52°), was purified by sublimation and recrystallised from light petroleum. The benzoyl compound, m.p. 89° (lit.,[21] 95—96°), was purified by chromatography (deactivated alumina) using a 1 : 1 mixture of chloroform and light petroleum as the eluent. The ligand 1-ethyl-4-phospha-3,5,8-trioxabicyclo[2,2,2]octane[22] for brevity will be referred to in this section by its trivial name trimethylol-propane phosphite. Chromatographic separations were carried out with a column of deactivated alumina (30 cm. × 1·8 cm.). The light petroleum referred to in these reactions had a boiling range of 30—40°. All gas volumes are given at s.t.p.

cis-*Benzoyltetracarbonyl(trimethylolpropane phosphite)-manganese.*—(a) *From phenylpentacarbonylmanganese.* Phenylpentacarbonylmanganese (1·05 g., 3·86 mmoles) and trimethylolpropane phosphite (0·80 g., 4·93 mmoles) in light petroleum (50 ml.) were sealed in a Dreadnought tube *in vacuo*. After 7 days at room temperature the tube was opened to give carbon monoxide (16·5 ml., 0·74 mmole) and a solution which was chromatographed. Elution with

[21] T. H. Coffield, J. Kozikowski, and R. D. Closson, *J. Org. Chem.*, 1957, **22**, 598.

[22] W. S. Wadsworth and W. D. Emmons, *J. Amer. Chem. Soc.*, 1962, **84**, 610.

light petroleum gave unchanged phenylpentacarbonyl-manganese (0·35 g., 1·30 mmoles, 35%). Elution with a 10 : 1 mixture of light petroleum and chloroform gave yellow crystals of cis-benzoyltetracarbonyl(trimethylolpropane phosphite)manganese (0·23 g., 0·56 mmole, 15%) (Found: C, 46·7; H, 3·8; P, 7·7. $C_{17}H_{16}MnO_8P$ requires C, 46·6; H, 3·7; P, 7·1%), which was recrystallised from methylene chloride and light petroleum. Finally, elution with a 1 : 1 mixture of light petroleum and chloroform gave yellow needles of cis-benzoyltricarbonylbis(trimethylolpropane phosphite)manganese (0·25 g., 0·46 mmole, 12%) (Found: C, 46·3; H, 4·8; P, 11·4%; M, 570. $C_{22}H_{27}MnO_{10}P_2$ requires C, 46·4; H, 4·8; P, 10·9%; M, 569), which was recrystallised from methylene chloride and light petroleum.

(b) From benzoylpentacarbonylmanganese. Benzoyl-pentacarbonylmanganese (0·83 g., 2·76 mmoles) and tri-methylolpropane phosphite (1·95 g., 12·1 mmoles) in methylene chloride (50 ml.) were sealed in a tube in vacuo. After 22 hr. at room temperature the tube was opened to give carbon monoxide (70 ml., 3·14 mmoles) and a yellow solution. Removal of the solvent and chromatography of the residual solid gave unchanged ligand (1·25 g., 7·70 mmoles, 60%) upon elution with light petroleum, and cis-benzoyltetracarbonyl(trimethylolpropane phosphite)manga-nese (0·74 g., 1·72 mmoles, 62%) upon elution with a 10 : 1 mixture of light petroleum and chloroform. Final elution with chloroform gave cis-benzoyltricarbonylbis(trimethylol-propane phosphite)manganese (0·67 g., 1·18 mmoles, 40%).

trans-Benzoyltetracarbonyl(trimethylolpropane phosphite)-manganese.—Octacarbonylbis(trimethylolpropane phos-phite)dimanganese (2·00 g., 3·04 mmoles; prepared by the reaction of decacarbonyldimanganese and an excess of trimethylolpropane phosphite in refluxing xylene for 2 hr. under an atmosphere of nitrogen) in dry tetrahydrofuran (20 ml.), was stirred for 3·5 hr. with 1% sodium amalgam (50 ml.) under an atmosphere of nitrogen. The excess of amalgam was removed from the solution, a solution of re-distilled benzoyl chloride (0·86 g., 6·10 mmoles) in tetra-hydrofuran (20 ml.) was added, and the mixture was stirred for 30 min. at room temperature. After removal of sodium chloride by filtration the solvent was removed under re-duced pressure, and the residue was chromatographed using a 1 : 5 mixture of chloroform and light petroleum as eluent to give trans-benzoyltetracarbonyl(trimethylolpropane phos-phite)manganese (0·22 g., 0·51 mmole, 8%) as pale yellow crystals recrystallised from methylene chloride and light petroleum (Found: C, 47·3; H, 3·6%; M, 434. $C_{17}H_{16}$-MnO_8P requires C, 47·0; H, 3·7%; M, 434). Further elution gave cis-benzoyltetracarbonyl(trimethylolpropane phosphite)manganese (1·92 g., 4·40 mmoles, 72%).

cis-Benzoyltricarbonylbis(trimethylolpropane phosphite)-manganese.—(a) From phenylpentacarbonylmanganese. Using the same general procedure as outlined in the preced-ing experiments, phenylpentacarbonylmanganese (1·00 g., 3·67 mmoles), trimethylolpropane phosphite (6·0 g., 36·7 mmoles), and methylene chloride (40 ml.) were kept at room temperature for 10 days in a sealed tube. Carbon monoxide (55 ml., 2·5 mmoles) was evolved and chromatography gave unchanged ligand (65%) and, after recrystallisation as before, cis-benzoyltricarbonylbis(trimethylolpropane phos-phite)manganese (1·43 g., 2·52 mmoles, 69%).

(b) From cis-benzoyltetracarbonyl(trimethylolpropane phos-phite)manganese. The infrared spectrum of a solution of cis-benzoyltetracarbonyl(trimethylolpropane phosphite)-

manganese (0·0205 g., 0·046 mmole) and trimethylolpropane phosphite (0·0956 g., 0·59 mmole) in chloroform (10 ml.) was observed in the metal carbonyl region during 2 days. After this period the absorptions due to the mono-substituted complex had completely disappeared, and the product had a spectrum identical with that of cis-benzoyl-tricarbonylbis(trimethylolpropane phosphite)manganese.

trans-Phenyltricarbonylbis(trimethylolpropane phosphite)-manganese.—Phenylpentacarbonylmanganese (1·00 g., 3·7 mmoles) and trimethylolpropane phosphite (2·00 g., 12·4 mmoles) were heated under reflux in chloroform (50 ml.) for 3 days under nitrogen (1 atm.). The solvent was re-moved under reduced pressure and the residual solid chromatographed. Elution with light petroleum gave unchanged ligand (0·97 g., 6·0 mmoles, 48%). Further elution with a 1 : 1 mixture of light petroleum and chloro-form gave white crystals of trans-phenyltricarbonylbis(tri-methylolpropane phosphite)manganese (1·40 g., 2·6 mmoles, 70%) [Found: C, 46·6; H, 5·5; P, 11·5. $C_{21}H_{27}MnO_9P_2$ requires C, 46·4; H, 5·0; P, 11·4%] which was recrystallised from light petroleum and methylene chloride.

Phenyltetracarbonyl(trimethylolpropane phosphite)manga-nese.—(a) From cis-benzoyltetracarbonyl(trimethylolpropane phosphite)manganese in the solid state. cis-Benzoyltetra-carbonyl(trimethylolpropane phosphite)manganese (1·00 g., 2·30 mmoles) was heated at 110° under nitrogen until evolution of carbon monoxide (37 ml., 1·65 mmoles) ceased. The residual solid, chromatographed using a 10 : 1 mixture of light petroleum and chloroform as the eluent, gave white crystals of a mixture of cis- and trans-phenyltetracarbonyl(trimethylolpropane phosphite)manganese (0·56 g., 1·40 mmoles, 61%) [Found: C, 46·9; H, 3·8; P, 7·9. $C_{16}H_{16}MnO_7P$ requires C, 47·2; H, 3·9; P, 7·6%], re-crystallised from methylene chloride and light petroleum. A small amount of starting material (10%) was recovered on further elution.

(b) In chloroform solution. cis-Benzoyltetracarbonyl(tri-methylolpropane phosphite)manganese (1·00 g., 2·30 mmoles) in chloroform (170 ml.) heated at 80° for 2 hr. in a sealed tube in vacuo, evolved carbon monoxide (44 ml., 1·97 mmoles). The solvent was then removed under re-duced pressure and the residue chromatographed. Elution with light petroleum gave phenylpentacarbonylmanganese (0·02 g., 0·07 mmole, 3%) identified by i.r. and mixed m.p. with an authentic sample. Elution with a 10 : 1 mixture of light petroleum and chloroform gave cis-trans-phenyl-tetracarbonyl(trimethylolpropane phosphite)manganese (0·74 g., 1·82 mmoles, 78%) and unchanged starting material (0·17 g., 0·39 mmole, 17%).

Action of Heat on cis-Benzoyltricarbonylbis(trimethylolpro-pane phosphite)manganese.—(a) In chloroform solution. Details of reactions carried out at different temperatures are given in Table 1. A typical reaction is described.

cis-Benzoyltricarbonylbis(trimethylolpropane phosphite)-manganese (1·46 g., 2·52 mmoles) in chloroform (100 ml.) was heated at 60° for 18·5 hr. in a sealed tube in vacuo. The solvent was then removed under reduced pressure and the solid remaining was chromatographed. Elution with a 10 : 1 mixture of light petroleum and chloroform gave trimethylolpropane phosphite (0·03 g., 0·17 mmole, 7%), cis-phenyltetracarbonyl(trimethylolpropane phosphite)-manganese (0·32 g., 0·79 mmole, 31%), and trans-phenyltri-carbonylbis(trimethylolpropane phosphite)manganese (0·16 g., 0·32 mmole, 12%) respectively. Elution with a 5 : 1 mixture of light petroleum and chloroform gave unchanged

starting material (0·23 g., 0·41 mmole, 16%). Finally, elution with chloroform gave pale yellow crystals of trans-*benzoyltricarbonylbis(trimethylolpropane phosphite)manganese* (0·61 g., 1·07 mmoles, 42%) [Found: C, 46·4; H, 4·7; P, 11·0%; M, 554. $C_{22}H_{27}MnO_{10}P_2$ requires C, 46·4; H, 4·8; P, 10·9%; M, 569] which was recrystallised from methylene chloride and light petroleum.

(b) *In the solid state.* cis-Benzoyltricarbonylbis(trimethylolpropane phosphite)manganese (3·1 g., 5·4 mmoles) was heated at 130° under nitrogen (1 atm.) until all evolution of carbon monoxide ceased. The residue was purified by chromatography and recrystallisation to give trans-phenyltricarbonylbis(trimethylolpropane phosphite)manganese (2·10 g., 3·9 mmoles, 72%).

trans-*Benzoyldicarbonyltris(trimethylolpropane phosphite)-manganese.*—Phenylpentacarbonylmanganese (3·00 g., 11·0 mmoles) and trimethylolpropane phosphite (7·5 g., 46·2 mmoles) were intimately mixed and heated for 3 days at 100° under an atmosphere of nitrogen. The product was chromatographed using light petroleum initially as the eluent to remove unchanged ligand. Elution with a 3 : 1 mixture of light petroleum and chloroform gave trans-phenyltricarbonylbis(trimethylolpropane phosphite)manganese (1·73 g., 3·2 mmoles, 29%), and trans-benzoyltricarbonylbis(trimethylolpropane phosphite)manganese (1·0 g., 1·8 mmoles, 16%). Final elution with chloroform gave a yellow solid (5·2 g.) which was re-chromatographed. Elution with a 5 : 1 mixture of light petroleum and chloroform gave a further quantity of trans-phenyltricarbonylbis-(trimethylolpropane phosphite)manganese (0·17 g., 0·30 mmole, 3%) and trans-benzoyltricarbonylbis(trimethylolpropane phosphite)manganese (1·63 g., 2·9 mmoles, 26%). Final elution with a 1 : 1 mixture of chloroform and light petroleum gave a product which was recrystallised from methylene chloride and light petroleum to give pale yellow crystals, the elemental analysis and i.r. spectrum of which showed that they contained methylene chloride. The product was recrystallised from acetone and light petroleum, then heated at 80° for 7 hr. under high vacuum, to liberate slowly associated acetone and methylene chloride to give pale yellow trans-*benzoyldicarbonyltris(trimethylolpropane phosphite)manganese* (1·0 g., 1·4 mmoles, 13%) [Found: C, 45·9; H, 5·2%; M, 702. $C_{27}H_{38}MnO_{12}P_3$ requires C, 46·2; H, 5·4%; M, 701].

Reaction of Phenyltetracarbonyl(trimethylolpropane phosphite)manganese with Trimethylolpropane Phosphite.—(a) *At room temperature.* cis-trans-Phenyltetracarbonyl(trimethylolpropane phosphite)manganese (0·50 g., 1·23 mmoles), trimethylolpropane phosphite (2·0 g., 12·3 mmoles), and chloroform (50 ml.) were sealed in a tube *in vacuo* for 6 days at room temperature. The reaction mixture was then chromatographed to give unchanged ligand (0·10 g., 0·61 mmole, 5%), and starting material (0·19 g., 0·45 mmole, 37%), and after recrystallisation cis-benzoyltricarbonylbis(trimethylolpropane phosphite)manganese (0·42 g., 0·73 mmole, 59%).

(b) *At* 60°. cis-trans-Phenyltetracarbonyl(trimethylolpropane phosphite)manganese (0·54 g., 1·32 mmoles), trimethylolpropane phosphite (0·29 g., 1·78 mmoles), and chloroform (50 ml.) were heated at 60° for 19·5 hr. in a sealed tube. Carbon monoxide (12·3 ml., 0·55 mmole) was evolved. The reaction mixture was chromatographed to give unchanged starting material (0·07 g., 0·02 mmole, 2%), cis-benzoyltricarbonylbis(trimethylolpropane phosphite)manganese (0·18 g., 0·31 mmole, 24%), trans-phenyl-

tricarbonylbis(trimethylolpropane phosphite)manganese (0·14 g., 0·27 mmole, 17%), and trans-benzoyltricarbonylbis-(trimethylolpropane phosphite)manganese (0·40 g., 0·71 mmole, 54%).

Decarbonylation of trans-*Benzoyltricarbonylbis(trimethylolpropane phosphite)manganese.*—trans-Benzoyltricarbonylbis(trimethylolpropane phosphite)manganese (0·36 g., 0·63 mmole) was heated in chloroform (20 ml.) in a sealed tube at 60° for 3 days. The solvent was removed under reduced pressure and the residue washed well with light petroleum to give trans-phenyltricarbonylbis(trimethylolpropane phosphite)manganese (0·33 g., 0·61 mmole, 97%).

Reaction of Phenylpentacarbonylmanganese with Triphenylphosphine.—Phenylpentacarbonylmanganese (1·50 g., 5·50 mmoles) and triphenylphosphine (1·40 g., 5·50 mmoles) in tetrahydrofuran (20 ml.), stirred for 4·5 hr. at room temperature, evolved carbon monoxide (22 ml., 1·0 mmole). Removal of the solvent gave a yellow residue which showed a strong absorbance at 1724 cm.$^{-1}$ in its i.r. spectrum. Vigorous gas evolution occurred when the residue was chromatographed using a 1 : 1 mixture of light petroleum and chloroform as eluent to give cis-phenyltetracarbonyl-(triphenylphosphine)manganese (1·50 g., 3·0 mmoles, 54%) as a yellow solid m.p. 137° (lit.,[1,2] 139°). Its i.r. spectrum was identical with that reported [1,2] and showed no strong band in the 1700—1750 cm.$^{-1}$ region.

Benzoyltetracarbonyl(triphenyl phosphite)manganese.—Phenylpentacarbonylmanganese (1·5 g., 5·5 mmoles) and triphenyl phosphite (1·7 g., 5·5 mmoles) in tetrahydrofuran (20 ml.) evolved carbon monoxide (25 ml., 0·7 mmole) when stirred for 5 hr. at room temperature under an atmosphere of nitrogen. The solvent was removed under reduced pressure and the residue was washed with light petroleum. Recrystallisation of the residue from light petroleum and methylene chloride gave yellow crystals of a mixture of cis- and trans-*benzoyltetracarbonyl(triphenyl phosphite)-manganese* (1·3 g., 2·2 mmoles, 40%) (Found: C, 59·5; H, 3·6%; M, 589. $C_{29}H_{20}MnO_8P$ requires C, 59·8; H, 3·4%; M, 582).

cis-*Phenyltetracarbonyl(triphenyl phosphite)manganese.*—trans-Benzoyltetracarbonyl(triphenyl phosphite)manganese (0·95 g., 1·63 mmoles) was heated at 100° under nitrogen until evolution of carbon monoxide (19·7 ml., 0·89 mmole) ceased. Chromatographic separation of the residue using light petroleum as an eluent gave cis-*phenyltetracarbonyl-(triphenyl phosphite)manganese* (0·31 g., 0·56 mmole, 34%) as a white crystalline solid, m.p. 85—86°, which was recrystallised from light petroleum (Found: C, 60·6; H, 3·7. $C_{28}H_{20}MnO_7P$ requires C, 60·6; H, 3·6%).

trans-*Benzoyltricarbonylbis(triphenyl phosphite)manganese.*—Phenylpentacarbonylmanganese (4·5 g., 16·5 mmoles) and triphenyl phosphite (11·0 g., 35·4 mmoles) in tetrahydrofuran (20 ml.), sealed in a Dreadnought tube *in vacuo*, and left for 3 days at room temperature, evolved carbon monoxide (186 ml., 8·3 mmoles). Removal of the solvent and chromatography of the residual solid using light petroleum as eluent gave triphenyl phosphite (4·0 g., 13·0 mmoles, 37%). Further elution with a 10 : 1 mixture of light petroleum and chloroform gave trans-*benzoyltricarbonylbis(triphenyl phosphite)manganese* (4·7 g., 5·5 mmoles, 33%) as golden yellow crystals, m.p. 135—136°, which were recrystallised from light petroleum and methylene chloride (Found: C, 64·0; H, 4·0%; M, 846. $C_{46}H_{35}MnO_{10}P_2$ requires C, 64·0; H, 4·1%; M, 864).

trans-*Phenyltricarbonylbis(triphenyl phosphite)manganese.*

—(a) *From phenylpentacarbonylmanganese.* Phenylpenta-carbonylmanganese (1·5 g., 5·5 mmoles) and triphenyl phosphite (4·65 g., 15 mmoles) in methylene chloride (15 ml.) were sealed for 7 days at room temperature in a Dread-nought tube *in vacuo.* Chromatographic separation of the products gave triphenyl phosphite (2·1 g., 6·8 mmoles, 45%) on elution with light petroleum. Further elution with a 20 : 1 mixture of light petroleum and chloroform gave trans-*phenyltricarbonylbis(triphenyl phosphite)manganese* (0·45 g., 0·53 mmole, 10%) as cream crystals, m.p. 137—138°, recrystallised from methylene chloride and light petroleum (Found: C, 64·8; H, 4·4%; M, 759. $C_{45}H_{35}$-MnO_9P_2 requires C, 64·6; H, 4·2%; M, 836). Final elution with a 5 : 1 mixture of light petroleum and chloroform gave *trans*-benzoyltricarbonylbis(triphenyl phosphite)manganese (2·4 g., 2·78 mmoles, 50%).

(b) *From* trans-*benzoyltricarbonylbis(triphenyl phosphite)-manganese.* *trans*-Benzoyltricarbonylbis(triphenyl phos-phite)manganese (2·05 g., 2·4 mmoles) was heated at 120° under nitrogen until evolution of carbon monoxide (54 ml., 2·4 mmoles) ceased. The remaining solid (2·00 g., 2·4 mmoles, 100%) was trans-phenyltricarbonylbis(triphenyl phosphite)manganese.

Dipole Moments.—The moments were evaluated using the equation [23]

$$\mu = [8·908 \times 10^{-39} \times M(\alpha_\epsilon - \alpha_\eta)]^{\frac{1}{2}}$$

where $\alpha_\epsilon = \Delta\epsilon/w$, $\alpha_\eta = \Delta_D\eta^2/w$, $w =$ weight fraction of solute, $\Delta\epsilon =$ the difference between the dielectric constant of the solution and that of benzene, and $\Delta_D\eta^2 =$ difference in refractive indices. Both α_ϵ and α_η were determined graphically. The instrument was calibrated using cyclo-hexane (ϵ 2·0228), benzene (ϵ 2·2825), and di-n-butyl ether (ϵ 3·0830) and was checked using phenyl- and benzoyl-pentacarbonylmanganese, for which values $\mu = 0·77 \pm 0·07$ D and $\mu = 2·38 \pm 0·02$ D respectively, compared favourably with the reported values.[16]

[23] G. Hedestrand, *Z. phys. Chem.,* 1929, **2**, 428.