The Reaction of Ligands with Phenyl- or Methyl-manganese Carbonyl

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METHYLMANGANESE CARBONYL reacts with carbon monoxide,[1] amines,[2,3] or triphenylphosphine[3] to give products of the type $CH_3{\cdot}CO{\cdot}Mn(CO)_4L$. It has been suggested[3] that triphenyl phosphite reacts similarly. Phenylmanganese carbonyl reacts with carbon monoxide[4] to give benzoylmanganese carbonyl. New data throw light on the mechanism of formation and the stereochemistry of these and related new complexes.

Whereas the monosubstituted complex $PhMn(CO)_4L$ is obtained when triphenyl-phosphine, -arsine, or -stibine react with phenylmanganese carbonyl in methylene chloride at room temperature, the ligands 1,2-bis(diphenylphosphino)-ethane, diphenyl methylphosphonite, and alkyl or aryl phosphites readily displace *two* carbon monoxides under the same reaction conditions to give the disubstituted complexes $PhMn(CO)_3L_2$ (see Table). The patterns of the terminal carbonyl stretching frequencies of the monosubstituted complexes are very similar to those reported[5,6] for the compounds *cis*-$X{\cdot}Mn(CO)_4{\cdot}PPh_3$, where X = CH_3, Cl, Br, or I, suggesting that in these complexes the phenyl group and substituting ligand L are *cis* to each other.

The proton magnetic resonance spectrum (measured in benzene) of the complex $PhMn(CO)_3L_2$ (L = diphenyl methylphosphonite) showed the methyl group as a 1:2:1 triplet (τ 8·27; J = 2 c./sec.), the methyl protons coupling equally with both phosphorus nuclei. This suggests[7] that the two ligands are in the *trans*-configuration. Comparison of the carbonyl stretching frequencies of this complex with those of the complexes obtained

[1] R. D. Closson, J. Kozikowski, and T. H. Coffield, *J. Org. Chem.*, 1957, **22**, 598; F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, 1962, **1**, 30.
[2] K. A. Kelbys and A. H. Filbey, *J. Amer. Chem. Soc.*, 1960, **82**, 4204.
[3] R. J. Mawby, F. Basolo, and R. G. Pearson, *ibid.*, 1964, **86**, 3996.
[4] R. D. Closson, J. Kozikowski, and T. H. Coffield, in "International Conference on Co-ordination Chemistry", Chem. Soc. Special Publ., 1959, **13**, 126.
[5] W. Hieber, G. Faulhaber, and F. Thenbert, *Z. anorg. Chem.*, 1962, **314**, 125.
[6] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1964, **86**, 5043, quoting results obtained by F. A. Cotton and C. S. Kraihanzel.
[7] J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 1963, 279.

from triphenyl phosphite and trimethyl phosphite (see Table) indicates that these complexes also have this stereochemistry.

Reaction of $PhMn(CO)_5$ *with ligands*

Ligand (L)	Product	M.p.	Carbonyl stretching frequencies (cm.$^{-1}$*)
Ph_3P	$PhMn(CO)_4L$	138—139°	2066s, 1992s, 1972s, 1949s
Ph_3As	,,	129—130	2066s, 1988s, 1976s, 1949s
Ph_3Sb	,,	105—106	2058s, 2016s, 1988s, 1969s
$Ph_2P.CH_2.CH_2.PPh_2$	$PhMn(CO)_3L_2$	176·5—177	1996s, 1919s
$(PhO)_3P$	,,	146·5—147·5	2016m, 1968s, 1934s
$(CH_3O)_3P$	,,	80·5—81	2083m, 2000s, 1980s
$(PhO)_2P.CH_3$	,,	173—174·5	2041m, 1961s, 1949s

Reaction of $CH_3{\cdot}Mn(CO)_5$ *with ligands*

Ligand (L)	Product	M.p.	Carbonyl stretching frequencies (cm.$^{-1}$)
Ph_3As	$CH_3.CO.Mn(CO)_4L$	79·5—80°	2054s, 2012s, 1988sh, 1969s, 1610s
Ph_3P	,,	108—109†	2066s, 2053sh, 1992s, 1961s, 1600s
Ph_3Sb	,,	101·5—102	2058s, 2012s, 1980sh, 1961s, 1595s
$Ph_2P.CH_2.CH_2.PPh_2$	$CH_3.CO.Mn(CO)_3L_2$	153—155	2053s, 1984s, 1953s, 1608s
$(PhO)_3P$	,,	146·5—147·5	2058m, 2000sh, 1976s, 1953s
$(PhO)_2P.CH_3$	,,	138—139	2049w, 1984s, 1912s

* CCl_4 solutions.
† Lit. m.p. 98°; terminal carbon–oxygen stretching frequencies 2066, 1995, 1959, and acetyl carbon–oxygen 1631 cm.$^{-1}$ in hexane.

monoxide *cis* to the ligand L would be displaced in the formation of the complexes $PhMn(CO)_3L_2$ *via* the complexes $PhMn(CO)_4L$. Examination of models suggests that this would be difficult sterically when the displacing ligand is triphenylphosphine, but possible with phosphites. In the reaction of $PhMn(CO)_5$ with phosphites a *cis*-complex is probably initially formed, which rearranges to the thermodynamically more stable *trans*-complex actually isolated.

Kinetic studies have shown that the rate of reaction in chloroform of phenylmanganese carbonyl with the monosubstituting ligands is independent of the ligand and ligand concentration. Therefore, since phenylmanganese carbonyl reacts with the ligand butadiene to form a benzoyl complex,[8] it is suggested that these reactions proceed *via* initial and rate-determining rearrangement to benzoylmanganese tetracarbonyl followed by rapid reaction with the ligand, then decarbonylation:

$$PhMn(CO)_5 \underset{}{\overset{slow}{\rightleftharpoons}} PhCO{\cdot}Mn(CO)_4 \xrightarrow{L,\ fast}$$

$$PhCO{\cdot}Mn(CO)_4L \xrightarrow[fast]{-CO} cis\text{-}PhMn(CO)_4L.$$

Recent experiments[6] with *trans*acetyltetracarbonyl(triphenylphosphine)manganese indicate that the postulated intermediate $PhCO{\cdot}Mn(CO)_4L$ has a *trans*-configuration. An attempt to obtain this complex by carbonylation of $PhMn(CO)_4{\cdot}PPh_3$ (20°, 200 atm.) led to the interesting displacement of the phosphine, probably *via* an insertion–elimination mechanism:

$$PhMn(CO)_4{\cdot}PPh_3 \rightarrow PhCO{\cdot}Mn(CO)_3{\cdot}PPh_3 \rightarrow PhMn(CO)_4 + PPh_3$$

$$PhMn(CO)_4 \xrightarrow{CO} PhMn(CO)_5 \xrightarrow{CO} PhCO{\cdot}Mn(CO)_5$$

If it is assumed that the *trans*-effect is important in octahedral manganese complexes, then carbon monoxide *cis* to the ligand L would be displaced...

Methylmanganese carbonyl in methylene chloride reacts at room temperature with triphenyl-phosphine, -arsine, or -stibine to give the monosubstituted acyl complexes $CH_3CO{\cdot}Mn(CO)_4L$, whereas triphenyl phosphite, 1,2-bis(diphenylphosphino)ethane, and diphenyl methylphosphonite under the same reaction conditions displace two carbon monoxides to give disubstituted acyl complexes. The presence of an acetyl group in the complex obtained with the bidentate ligand can be verified from the infrared spectrum, but the relevant region for the acetyl group in the spectra of the other two disubstituted complexes is masked.

Basolo *et al.* have reported that the complex $CH_3{\cdot}CO{\cdot}Mn(CO)_4{\cdot}PPh_3$, obtained from the reaction of methylmanganese carbonyl with triphenylphosphine, has a *trans*-configuration.[6] Comparison

[8] W. D. Bannister, M. Green, and R. N. Haszeldine, *Proc. Chem. Soc.*, 1964, 370.

of the carbonyl stretching frequencies of the similar complexes obtained from triphenyl-arsine and -stibine suggests that these complexes have the same stereochemistry.

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