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Preliminary communication

Factors limiting higher substitution of manganese pentacarbonyl bromide

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SUMMARY

Successive substitution of [$Mn(CO)_5Br$] with phosphines and phosphites (L) have been shown to be dependent upon the size of L and the stereochemistry of the manganese complex.

A notable feature of the extensive studies on halomanganese pentacarbonyl bromide with a variety of monodentate tertiary alkyl or aryl phosphorus ligands is that substitution of more than two carbonyl groups has been obtained for one ligand only, *viz.* $P(OMe)_3$[1]. This was attributed to the "carbonyl-like" π-acceptor properties of the ligand coupled with its low steric requirements. By refluxing [$Mn(CO)_5Br$] with three molar equivalents of sterically favourable ligands, L, in benzene, we have prepared a series of compounds *mer*-[$Mn(CO)_2L_3Br$], (III) (L = $P(OEt)_3$, PMe_3, PMe_2Ph and $AsMe_2Ph$) which suggest that higher carbonyl substitution of [$Mn(CO)_5Br$] is little affected by the electronic properties of L but requires: (i) a CO group bonded *trans* to a similar group; (ii) that L is small.

For example, a qualitative investigation of the reaction between [$Mn(CO)_5Br$] and PMe_3 (L) in refluxing benzene has given the reaction scheme depicted in Fig.1.

The slow reaction of I with excess PMe_3 to give III can be linked with earlier studies[2] on the rate of isomerisation of I to II [L = PBu_3 and $P(OBu)_3$] which have shown this rate to be suppressed by free ligand in solution. For L = PMe_3 the reaction times show that isomer II, in which the CO groups are mutually *trans*, is more reactive towards L than I and we are studying quantitatively the possibility that the direct reaction I→III proceeds entirely via II with the excess ligand retarding the rate-determining isomerisation I→II.

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TABLE 1

PHYSICAL DATA FOR SOME SELECTED MANGANESE CARBONYL COMPLEXES

Compound[a]	*Carbonyl stretching frequencies (cm^{-1})*
fac-[$Mn(CO)_3(PMe_3)_2Br$] (I)	2024 s, 1952s, 1901 s[d]
mer-[$Mn(CO)_3(PMe_3)_2Br$] (II)	2033 w, 1944 s, 1900 m[d]
mer-[$Mn(CO)_2(PMe_3)_3Br$] (III)	1929 s, 1846 s[b]
mer-[$Mn(CO)_2(PMe_2Ph)_3Br$][e] (III)	1929 s, 1851 s[d]
mer-[$Mn(CO)_2(AsMe_2Ph)_3Br$] (III)	1931 s, 1852 s[b]
mer-[$Mn(CO)_2\{P(OEt)_3\}_3Br$] (III)	1973 s, 1888 s[d]
trans-[$Mn(CO)_2\{P(OEt)_3\}_3Br$] (IV)	2012 w, 1920 s[c]
trans-[$Mn(CO)_2\{P(OMe)_3\}_3Br$] (IV)	2010 w, 1916 s[c]

[a] Satisfactory analyses have been obtained for all compounds reported here.
[b] In chloroform
[c] In dichloromethane
[d] In benzene
[e] This compound has been prepared indirectly elsewhere[7].

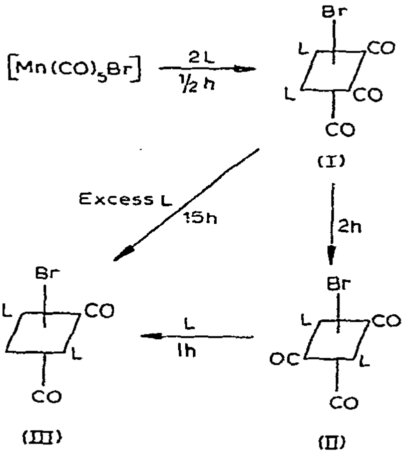

Fig.1.

The reduced reactivity of an isomer containing *cis*-CO groups is also demonstrated by the failure to induce further substitution in all compounds III prepared here. By contrast, *trans*-[$Mn(CO)_2\{P(OMe)_3\}_3Br$], (IV) (obtained by the reaction scheme depicted in Fig. 2) readily reacts with $P(OMe)_3$, using a 20 molar excess in refluxing light petroleum ether (b.p. 60–80°), giving a 50% conversion to the known[1] tetrasubstituted species [$Mn(CO)\{P(OMe)_3\}_4Br$] within 10 min.

With longer reaction times, isomerisation of IV to the more stable III occurs, which terminates the reaction since III is unreactive towards $P(OMe)_3$. Thus the relative stability of certain isomers towards isomerisation can be a limitation to further substitution and could explain why mild carbonyl substitution reactions of [$M(CO)_6$], (M = Cr, Mo, W), with monodentate phosphines and arsines usually terminate with *fac*-[$M(CO)_3L_3$][4].

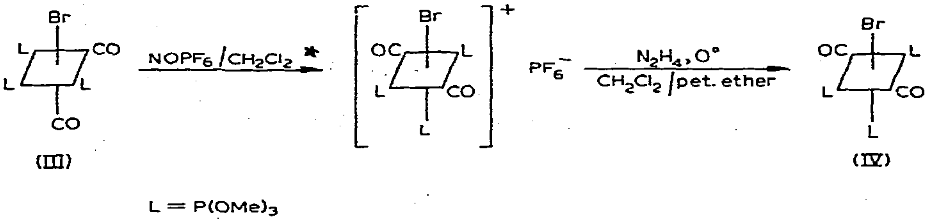

Fig.2.

The effect of ligand size on substitution reactions is demonstrated by our carbonylation reactions. We find that treatment of an acetone solution of III with CO under ambient conditions readily gives II, for all ligands L used here, at a rate dependent upon the size of L. Reaction times range from under 2 min [L = $AsMe_2Ph$ and PMe_2Ph] to 4 h [L = $P(OMe)_3$]. It was not possible to carbonylate I and II under similar conditions. Thus it seems that as steric crowding in the molecule increases, the rate of recombination of CO in an L–CO competing environment could become the dominant factor. Recent work by Tolman[5] has shown that although stable [NiL_4] (L = phosphine or phosphite) complexes can be readily prepared, they cannot be prepared by substitution of [$Ni(CO)_4$] with L. Hence for large ligands L it is not unlikely that higher substituted species are transiently formed in a reaction solution. An example is our reaction of [$Mn(CO)_5Br$] with an excess of the large phosphite $P(OPh)_3$ in refluxing benzene solution, which proceeds only as far as a dynamic equilibrium mixture of II and III although for the larger rhenium atom, [$Re(CO)_2\{P(OPh)_3\}_3Br$] is readily formed from [$Re(CO)_5Br$][6].

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★ For examples of this technique see ref. 3.