

PRELIMINARY COMMUNICATION

TRIMETHYLPHOSPHITE MANGANESE CARBONYL COMPLEXES

P.M. TREICHEL and J.J. BENEDICT

The Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (U.S.A.)

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The reaction of trimethylphosphite (L) with methylmanganese pentacarbonyl at 25° has been shown to give initially *cis*-CH₃COMn(CO)₄L, which slowly converts to a mixture of the *cis* and *trans* isomers¹. On standing, or more quickly on refluxing, a further substitution occurs to give one isomer CH₃COMn(CO)₃L₂★, (probably *fac*) which converts to a second isomer, *mer*(*trans*-L)-CH₃COMn(CO)₃L₂. This acyl compound in turn slowly decarbonylates to *mer*(*trans*-L)-CH₃Mn(CO)₃L₂².

We have now observed that further substitution of carbon monoxide by trimethylphosphite is possible in these systems. If CH₃COMn(CO)₃L₂ and trimethylphosphite in refluxing benzene are irradiated with ultraviolet light, one observes by monitoring the infrared spectrum first rapid decarbonylation and then further substitution to give CH₃Mn(CO)₂L₃ (65% yield after 2 days) and finally CH₃Mn(CO)L₄ (45% after 6 days) compounds★★. No intermediate acetyl compounds were observed in these reactions. The products are easily obtained in pure form from the crude reaction mixture by crystallization. Our preliminary observations are that the phosphite ligands are fairly easily displaced by carbon monoxide; reactions of both compounds at 50° with CO under a pressure of 300 psig converted each to CH₃COMn(CO)₃L₂ in high yield.

These new manganese compounds react quickly with a stoichiometric amount of bromine in CCl₄ at -8° and form the new compounds Mn(CO)₂L₃Br (75%) and Mn(CO)L₄Br (77%). The new compound Mn(CO)₃L₂Br is also obtainable in this way (75%). Interestingly the first compound, Mn(CO)₂L₃Br, is also formed directly from Mn(CO)₅Br and excess trimethylphosphite in refluxing benzene (30 h, 85% yield). This contrasts to the many reported reactions of Mn(CO)₅Br with phosphines, and also with triphenyl- and tributylphosphite, which give only disubstitution⁴.

We have run preliminary experiments which show that Mn(CO)₂L₃Br with sodium amalgam in tetrahydrofuran is rapidly converted to an anion, presumably Mn(CO)₂L₃⁻, which reacts with CH₃I to give CH₃Mn(CO)₂L₃ in high yield. Similar reactions are known for Mn(CO)₃(phos)₂Br compounds [phos = (C₆H₅)₃P, (C₆H₅O)₃P, P(C₆H₁₁)₃]⁵.

★If decarbonylation to CH₃Mn(CO)₄L precedes this substitution then the substitution reaction which follows must be fast, since no CH₃Mn(CO)₄L is seen by NMR monitoring². However for reactions with the constrained phosphite P(OCH₂)₃CCH₃, CH₃Mn(CO)₄L can apparently be identified as an intermediate³.

★★Satisfactory analyses have been obtained for all new compounds.

TABLE 1
DATA ON TRIMETHYLPHOSPHITE MANGANESE COMPOUNDS

Compound	Color	m.p. (°C)	IR $\nu(\text{CO})^a$	^1H NMR (τ) ^b
$\text{Mn}(\text{CO})_3\text{L}_2\text{Br}$	orange	110	2052w, 1975s, 1939m	6.19 (5.5 cps triplet)
$\text{Mn}(\text{CO})_2\text{L}_3\text{CH}_3$	white	117	1946s, 1860s	CH_3 10.54 (9.4 cps quartet) $(\text{CH}_3\text{O})_3\text{P}$ 6.33 (4.5 cps triplet like) ^c
$\text{Mn}(\text{CO})_2\text{L}_3\text{Br}$	orange	161	1980s, 1898s	6.22 (4.8 cps triplet like) ^c
$\text{Mn}(\text{CO})\text{L}_4\text{CH}_3$	white	176	1835s	CH_3 10.60 (8.5 cps quintuplet) $(\text{CH}_3\text{O})_3\text{P}$ 6.45 (broad singlet)
$\text{Mn}(\text{CO})\text{L}_4\text{Br}$	orange	131	1865s	6.29 (broad singlet)
$\text{Mn}(\text{CO})_2\text{L}_3^-$	not isolated		1954s, 1890s	

^a CHCl_3 solution. ^b ν_{s} . TMS internal standard. ^cThese resonance signals are not 1:2:1 triplets, but are somewhat similar in appearance.

Since for $\text{RMn}(\text{CO})\text{L}_4$ and $\text{RMn}(\text{CO})_2\text{L}_3$ ($\text{R} = \text{CH}_3, \text{Br}$), respectively, one and two $\nu(\text{CO})$ bands were observed, we conclude that in each case one isomer is formed (Table 1). The assigned C_{4v} symmetry of $\text{RMn}(\text{CO})\text{L}_4$ (Fig.1) seems reasonable since the proton NMR of the methyl compound shows the methyl group resonance as a regular quintuplet with equivalent coupling to the four phosphorus atoms. The assignment of geometry of the $\text{RMn}(\text{CO})_2\text{L}_3$ compounds is less straightforward, but of the three possible isomers we prefer the structure given in Fig.1 (C_3) having phosphite groups *cis* to R. This assignment is analogous to the established geometry of $\text{RMn}(\text{CO})_3\text{L}_2$ and $\text{RMn}(\text{CO})\text{L}_4$ compounds in which phosphite ligands are also *cis*- to the CH_3 -group. The quartet CH_3 proton resonance is somewhat reassuring, in that *cis* phosphorus atoms (although different) would probably have similar coupling constants with the CH_3 protons; if one phosphorus were *trans* then a substantially different P- CH_3 coupling constant value would seem more likely, and a CH_3 NMR pattern of two triplets would result. Of the two other possible isomers, one, having *trans* CO groups, (C_{2v})

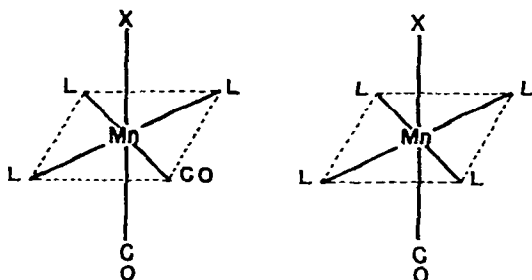


Fig.1. Proposed stereochemistry for $\text{Mn}(\text{CO})_2\text{L}_3\text{X}$ and $\text{Mn}(\text{CO})\text{L}_4\text{X}$ ($\text{X} = \text{Br}, \text{CH}_3$)

can be eliminated on the basis of the $\nu(\text{CO})$ intensities; the other (C_s) remains as a possibility though as we observed above, less likely.

No reactions have been reported to give substitution of more than two carbonyls from $\text{RMn}(\text{CO})_5$ ($R = \text{alkyl, aryl}$) compounds, and only in a few situations has substitution of more than two carbonyls been observed in manganese carbonyl halide systems. The most obvious cases of polysubstitution are the reactions of $\text{Mn}(\text{CO})_5\text{X}$ and isocyanides, reported to give $\text{Mn}(\text{CO})_{5-n}\text{L}_n\text{X}$ compounds ($n = 2-5$)⁶, and reactions of $\text{Mn}(\text{CO})_5\text{X}$ with 1,2-bis(diphenylphosphino)ethane (diphos)⁷ and a chelating tetra-phosphine⁸ to give cationic products $\text{MnL}_4(\text{CO})_2^+$. Hence these reactions are rather exceptional. We suspect now that trimethylphosphite is probably a ligand somewhat unique in its behavior. Phosphites are characterized as particularly good ligands for low-valent metal complexes.

Infrared studies on substituted complexes show phosphites to be somewhat more like CO or PF_3 than commonly used alkyl or aryl phosphines⁹. Furthermore trimethylphosphite must have rather low steric requirements. We might anticipate, therefore, somewhat more facile ligand replacement reactions involving this ligand. Several other reported reactions appear to substantiate this^{10,11}

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