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**Preliminary communication**

# The crystal and molecular structure of *trans*-bis(diphenylmethylphosphine)tricarbonyl manganese hydride

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## SUMMARY

The phosphine ligands in $HMn(CO)_3(PMePh_2)_2$ are *trans*-substituted; the *trans* pair of CO groups are markedly distorted from colinearity.

Recent work[1] on compounds of the type $Mn_2(CO)_8L_2$ has shown that the ligands are attached diaxially for L = $PPh_3$, $PMePh_2$ and $AsPh_3$ but are diequatorial when L = $AsMe_2Ph$. The analogous rhenium compounds have been prepared[2] and have been shown to react with excess ligand when irradiated with UV light to yield compounds $Re_2(CO)_7L_3$. Thermal reaction of $Mn_2(CO)_{10}$ with excess ligand yields $Mn_2(CO)_9L$, $Mn_2(CO)_8L_2$, paramagnetic $Mn(CO)_4L$, and $Mn(CO)_3L_2H$ (formed by abstraction of hydrogen from the solvent)[3]. Compounds $M(CO)_3L_2R$ where M = Re or Mn, L = substituted arsine or phosphine, R = H, halide or alkyl, have been reported in *trans* and *cis* (facial and meridial) forms, and certain of them have been shown to be labile to rearrangement[4]. The determination of the true stereochemistry of one of the derivatives $Mn(CO)_3L_2R$ was thus of interest.

Treatment of $Mn_2(CO)_{10}$ with a large excess of $PMePh_2$ in refluxing petroleum ether (b.p. 100–120°) for 12 h, followed by recrystallization from ether–ethanol yielded $HMn(CO)_3(PMePh_2)_2$. This compound is however more easily formed by treating $Mn_2(CO)_{10}$ with $PMePh_2$ in refluxing n-propanol. The 2000 $cm^{-1}$ region of the IR

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spectrum is similar to that recorded[3] for $HMn(CO)_3(PPh_3)_2$, with one very strong band at 1910 cm$^{-1}$ typical of a *trans*-disubstituted molecule, but with additional weaker bands at 2000 and 1960 cm$^{-1}$. The $^1H$ NMR spectrum (Me $\tau$ 7.92 (doublet), $J$(P—H) 7.2; Hydride 17.38 (triplet), $J$(P—H) 33; solvent $CD_2Cl_2$) supports this stereochemistry but is not unequivocal because a *trans* configuration is expected[5] to give a triplet for the methyl hydrogens.

$HMn(CO)_3(PMePh_2)_2$ forms well-shaped yellow monoclinic crystals, space group $C2/c$; $a$ = 16.79; $b$ = 17.20, $c$ = 19.03 (± 0.01 Å), $\beta$ 106.0 (± 0.1°), $Z$ = 8. No required molecular symmetry.

Three dimensional intensity data were measured on a Hilger & Watts four-circle diffractometer with Mo-$K_\alpha$ radiation. The positions of the heavy atoms were readily deduced from a Patterson map, and the lighter atoms were located from the subsequent Fourier maps. The structure has been refined[6] isotropically by block-diagonal least squares to $R$ 0.10 for 3800 data; refinement is continuing. The hydrogen atom was located as a very low peak in the electron density map: Mn—H 1.5 Å.

The two phosphine ligands are *trans* substituted (Fig. 1). Mn—P(1) 2.253, Mn—P(2) 2.257 Å, angle P—Mn—P 175°; average Mn—C, 1.78, C—O 1.17, P—C 1.86 Å.

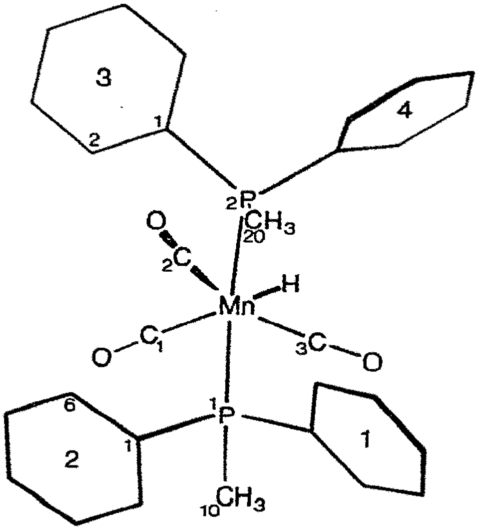

Fig. 1. Projection of the $HMn(CO)_3(PMePh_2)_2$ molecule down the $c$ axis.

While the $Mn(CO)_3$ portion of the molecule is coplanar within 0.01 Å, the *trans* pair of CO groups are bent toward the H atom; the C(2)—Mn—C(3) angle is 153°. This large distortion from linearity accounts for the additional peaks observed in the CO stretching region of the infrared absorption spectrum[7]. This distortion allows a decrease of compression strain between the *cis* pairs of CO groups; intramolecular average C···C distance 2.79 Å compared with 2.48 (± 0.06 Å for 8 contacts) in $Mn_2(CO)_8(PPh_2Me)_2$[1].

Both phosphine ligands show similar distortions; Mn—P(1)—C(2;1) 121°, Mn—P(2)—C(3;1) 120°, all other Mn—P—C angles 114°; C(3;1)—P(2)—C(20) 99°, C(2;1)—P(1)—C(10) 99°, all other C—P—C angles 102°. These distortions are due to short intramolecular separations between a phenyl ring and a CO group; C(2)· · ·C(2;6) 3.21 Å, C(1)· · ·C(3;2) 3.47 Å; these compressions are also reflected as small angular distortions about the manganese atom: P(1)—Mn—C(2) 93°, P(2)—Mn—C(1) 92°. Similar, although smaller distortions have been observed in related compounds[1].

The $MnP_2(CO)_3$ skeleton is distorted from square pyramidal towards trigonal bipyramidal, which implies that the paramagnetic species $Mn(CO)_4(PPh_2Me)$ will almost certainly be trigonal bipyramidal with the phosphine ligand oriented axially.

The atoms Me(20)—P(2)—Mn—P(1)—Me(10) are close to coplanar, with the two methyl groups *cis* oriented. This arrangement together with the restricted rotation about the Mn—P bonds probably accounts for the simple doublet observed in the NMR spectrum for the methyl protons.

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