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Preliminary communication

The crystal and molecular structure of dimethylphenylphosphine dimanganese(0) nonacarbonyl: $Mn_2(CO)_9(PMe_2Ph)$

MICHAEL LAING
Chemistry Department, University of Natal, Durban (South Africa)

ERIC SINGLETON and ROLF REIMANN
National Chemical Research Laboratory, CSIR, Pretoria (South Africa)

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SUMMARY

The phosphine ligand in $Mn_2(CO)_9(PMe_2Ph)$ is attached axially.

A recent study[1] has shown that the arsine ligands in $Mn_2(CO)_8(AsMe_2Ph)_2$ are attached equatorially while the phosphine ligands in $Mn_2(CO)_8(PMePh_2)_2$ are attached axially. In the light of the above results, the fact that scale Leybold models of the mono-substituted molecule can be constructed with the ligand in the equatorial position and that the compound $Re_2(CO)_9(PMe_2Ph)$ is the equatorial isomer[2], it seemed desirable to confirm that compounds $Mn_2(CO)_9L$ are in fact axially substituted[3]. The compounds $Mn_2(CO)_9L$, L = PMe_2Ph, $AsMe_2Ph$ have been prepared and shown to be isostructural[4] (superimposable infrared absorption spectra in the 2000 cm^{-1} region in solution); the structure determination of the phosphine derivative was undertaken.

The golden yellow crystals were monoclinic; space group $C2/c$; a 23.656, b 13.123, c 13.715 Å (± 0.005 Å) β 99.89° (± 0.05°), V 4194 Å^3, D_m 1.60 g·cm^{-3}, D_c 1.61 g·cm^{-3}, $Z = 8$; no required molecular symmetry. Intensity data were collected on a Philips four circle diffractometer using Zr-filtered Mo-K_α radiation. The heavy atoms were located from a three-dimensional Patterson map, and the lighter atoms were located in the subsequent Fourier map. The structure has been refined isotropically by block diagonal least-squares to $R = 0.09$ for 1640 observed data. Further refinement[5] is continuing.

The phosphine ligand is attached axially (Fig. 1). The atoms P-Mn(2)-Mn(1)-C(1)-O(1) are closely colinear.

The two $Mn(CO)_4$ groups are staggered with an average CMnMnC torsion angle of 45°. The bond lengths Mn–Mn 2.904, Mn–P 2.239, average Mn–C 1.76, C–O 1.17, P–C(Me) 1.86, and P–C(Ph) 1.79 Å are normal. The eight equatorial CO groups are bent

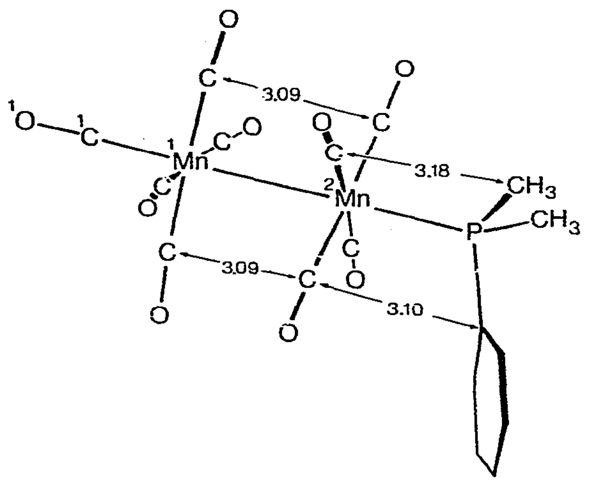

Fig. 1. A projection of $Mn(CO)_9(PMe_2Ph)$ down the y axis.

inwards toward the Mn—Mn bond, average Mn—Mn—C angle 87.5° with the oxygen atoms bent back slightly, average Mn—C—O 177.5° resulting in a geometry similar to that found in the diaxial $Mn_2(CO)_8L_2$ compounds[1,6]. The (PMe_2Ph) group is essentially undistorted, average angles Mn—P—C 114 (± 1°), C—P—C 104 (± 0.5°). This is in marked contrast with both of the $(PMePh_2)$ groups in $HMn(CO)_3(PMePh_2)_2$ [7] and to a lesser extent in $Mn_2(CO)_8(PMePh_2)_2$, where there are marked angular distortions caused by non-bonded intramolecular contacts with two of the carbonyl groups.

These results pose a new problem: how and why does the diequatorially substituted compound $Mn_2(CO)_8(AsMe_2Ph)_2$ form, when the compound $Mn_2(CO)_9(AsMe_2Ph)$ is apparently axially substituted? Not only must a rather radical rearrangement take place, but the diequatorial product that is produced is far more overcrowded and distorted than the hypothetical diaxial isomer. In addition, it is still possible that equatorial isomers of $Mn_2(CO)_9L$ can exist.

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