Crystal and Molecular Structures of Bis{tetracarbonyldiphenylmethylphosphinemanganese(0)} and Bis{tetracarbonyldimethylphenylarsinemanganese(0)}

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Summary In the molecule $[Mn_2(CO)_8(PMePh_2)_2]$, the phosphine ligands are attached axially, but in $[Mn_2(CO)_8(AsMe_2Ph)_2]$ the arsine ligands are attached equatorially.

In a study[1] of substitution reactions of manganese carbonyl compounds we find that $Mn_2(CO)_{10}$ reacts with two molar equivalents of L (L = $PMePh_2$ and $AsMe_2Ph$) in benzene solution under u.v. irradiation to give mixtures of $[Mn_2(CO)_9L]$ and $[Mn_2(CO)_8L_2]$, which may be separated chromatographically. The solid state and solution i.r. spectra of $[Mn_2(CO)_8(AsMe_2Ph)_2]$ contain a number of strong (CO) absorption bands implying that the ligands were substituted equatorially rather than axially.[2] The solution i.r. spectrum of $[Mn_2(CO)_8(PMePh_2)_2]$ is typical of a diaxially substituted compound; however, the solid state i.r. spectrum is similar to that of $[Mn_2(CO)_8(AsMe_2Ph)_2]$, suggesting that a rearrangement may have taken place as the compound crystallised yielding the diequatorially substituted compound, a most unusual occurrence. Because diequatorial substitution by simple monodentate ligands had not been reported previously for compounds of the type $Mn_2(CO)_8L_2$, crystal structure analyses of both compounds were undertaken.

Crystal data: $[Mn_2(CO)_8(PMePh_2)_2]$, monoclinic, space group $P2_1/c$; $a = 15{\cdot}39$, $b = 8{\cdot}49$, $c = 26{\cdot}15$ Å, $\beta = 95{\cdot}7°$, $U = 3401$ Å^3, $D_m = 1{\cdot}42$, $D_c = 1{\cdot}41$ g cm^{-3}, $Z = 4$, $M = 734$. No required molecular symmetry. $[Mn_2(CO)_8(AsMe_2Ph)_2]$, monoclinic, space group $C2/c$; $a = 10{\cdot}75$, $b = 13{\cdot}94$, $c = 18{\cdot}49$ Å, $\beta = 98{\cdot}15°$, $U = 2743$ Å^3, $D_m = 1{\cdot}68$, $D_c = 1{\cdot}69$ g cm^{-3}, $Z = 4$, $M = 698$. Molecular symmetry = 2.

For both compounds, three-dimensional integrated intensity data were collected by the multiple-film equi-inclination Weissenberg method with Ni-filtered Cu-K_α radiation and measured with a densitometer. The heavy atoms were located from three-dimensional temperature-sharpened Patterson maps, and the lighter atoms were located in the subsequent Fourier maps. The structures were refined isotropically by block diagonal least-squares: for $[Mn_2(CO)_8(PMePh_2)_2]$, $R = 0{\cdot}11$, 2930 observed data; for $[Mn_2(CO)_8\ (AsMe_2Ph)_2]$, $R = 0{\cdot}09$, 1030 observed data. All computations were done with local programs;[3] further refinement is continuing.

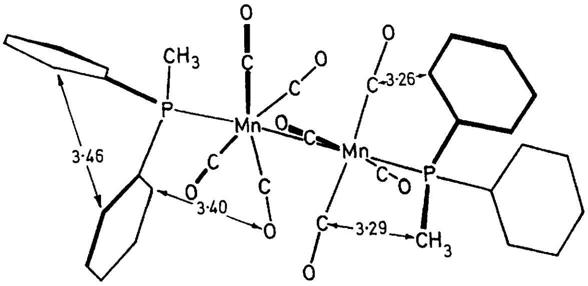

FIGURE 1. $Mn_2(CO)_8(PMePh_2)_2$ *a projection down* b.

In $[Mn_2(CO)_8(PMePh_2)_2]$, the two phosphine ligands are attached axially (Figure 1). The two $Mn(CO)_4$ groups are staggered with an average CMnMnC torsion angle of 45°, the overall geometry is thus similar to that of $[Mn_2(CO)_8(PEt_3)_2]$.[4] The bond-lengths are quite normal: Mn–Mn 2·90, Mn–P 2·23; average Mn–C 1·75, C–O 1·19, P–C 1·83 Å, C–P–C 102°. The eight CO groups are bent inward toward the Mn–Mn bond, average Mn–Mn–C angle 86°, with the oxygen atoms bent back slightly, average Mn–C–O angle 176°. The orientation of the phenyl rings is dictated by the non-bonded contacts between the *ortho-* hydrogen atoms and the CO groups.

The $[Mn_2(CO)_8(AsMe_2Ph)_2]$ molecule possesses a 2-fold axis perpendicular to the Mn–Mn bond, with the arsine groups attached to the manganese atoms in the equatorial position (Figure 2). The bond lengths Mn–Mn 2·94 Å, Mn–As 2·46 Å are close to the values of 2·97 and 2·40 Å observed in $[Mn_2(CO)_8f_4fars]$.[5] While in the latter molecule the $Mn(CO)_3$ As groups are almost perfectly staggered, in $[Mn_2(CO)_8(AsMe_2Ph)_2]$ the equatorial groups are closer to eclipsed. Average Mn–C 1·78, C–O 1·16, As–C 1·96 Å, C–As–C 101°. There are marked angular distortions in the molecule: Mn–Mn–As 103°, Mn–As–C(5) 124°, Mn–Mn–C(2) 168°, Mn–Mn–C(3) 79°, Mn–C(3)–O(3) 168°, Mn–C(4)–O(4) 171°. These are caused by the close contacts between the phenyl ring and two of the carbonyl groups (Figure 2).

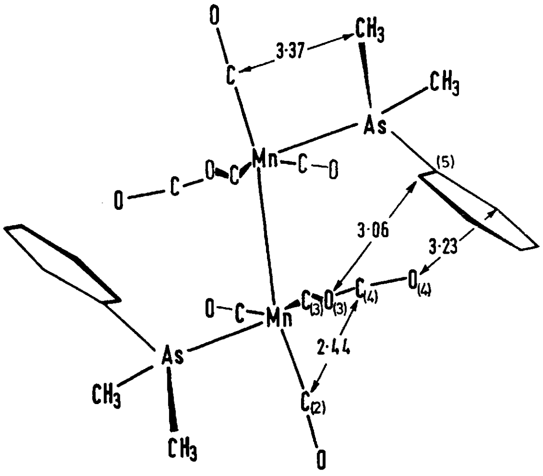

FIGURE 2. $Mn_2(CO)_8(AsMe_2Ph)_2$ *a projection down* b.

The crucial difference between the substitution properties of the phosphine and arsine ligands is caused by the Mn–As and As–C bond lengths being longer than the Mn–P and P–C lengths, which effectively reduces the repulsion between the substituent groups and the carbonyls and hence allows the statistically favoured equatorial substitution to take place in the diarsine complex.

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