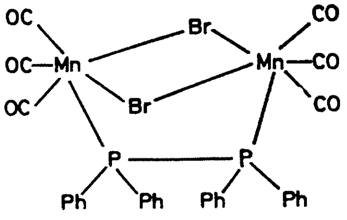
Studies on Organometallic Compounds with Hetero Multiple Bridges. X-Ray Crystal and Molecular Structure of $Mn_2Br_2(CO)_6P_2Ph_4$, the Product Resulting from Co-ordinative Addition of P_2Ph_4 to Manganese(I)

By JAMES D. KORP and IVAN BERNAL*
(*Chemistry Department, University of Houston, Houston, Texas* 77004)
JERRY L. ATWOOD and W. E. HUNTER
(*Chemistry Department, University of Alabama, University, Alabama* 35486)
and FAUSTO CALDERAZZO* and DARIO VITALI
(*Istituto Chimica Generale, University of Pisa, Via Risorgimento* 35 56100 *Pisa, Italy*)

Summary The P_2Ph_4- and Br-bridged compound $Mn_2Br_2(CO)_6P_2Ph_4$ (**3**) is the product of the reaction between $MnBr(CO)_5$ and P_2Ph_4 at reflux temperature in benzene.

WE have shown previously that the reactions of $Re_2Br_2(CO)_6(thf)_2$[1] (thf = tetrahydrofuran) with E_2R_2 (E = S[2,3] or Se[4]) and with P_2Ph_4[5] yield complexes of general formulae $Re_2Br_2(CO)_6E_2R_2$ (**1**) and $Re_2Br_2(CO)_6P_2Ph_4$ (**2**), respectively; all the complexes contain two hexaco-ordinated rhenium atoms surrounded by a *fac* set of carbonyl groups, two bridging bromides and uncleaved E–E or P–P bonds. Although oxidative addition across the E–E or P–P bond might be expected to be the preferred process,[6] the failure to observe it in the case of rhenium(I) is hardly surprising since the reluctance of low-spin d^6 configurations to lose one electron is well known. However, in the case of manganese, the presumably smaller ligand field and higher spin-pairing energy should be less unfavourable for the $d^6 \rightarrow d^5$ conversion. Contrary to these expectations and to an earlier suggestion,[7] it has now been found that $Mn_2Br_2(CO)_6P_2Ph_4$ (**3**), the product of the reaction[7] of $MnBr(CO)_5$ with P_2Ph_4 in refluxing benzene, has substantially the same molecular structure as that of the related rhenium complex (Figure). The red-brown diamagnetic complex (**3**) (χ_M^{corr} = $+53 \times 10^{-6}$ c.g.s.u., diamagnetic correction = -353×10^{-6} c.g.s.u.) was recrystallised from benzene ($\tilde{\nu}_{CO}$ in CCl_4, 2052ms, 2037ms, 2018w, 1971s, 1966s, and 1931vs cm^{-1}). *Crystal Data: M* 808·09, triclinic, a = 10·874(8), b = 11·841(9), c = 12·444(9) Å, α = 96·59(4), β = 100·55(5), γ = 95·37(4)°, U = 1554 Å,[3] Z = 2, D_m = 1·73, D_c = 1·73 g cm^{-3}, μ(Mo-K_α) = 34·2 cm^{-1}, space group = $P\bar{1}$. Intensities were recorded on an Enraf-Nonius CAD-4 diffractometer using the θ–2θ scan technique.†



(3)

All reflections occurring in the region 2° $\leqslant 2\theta \leqslant$ 50° were recorded; 3686 reflections were considered observed [$I \geqslant 3\sigma(I)$]. The structure was solved by Patterson and difference Fourier techniques, and refined to conventional $R(F)$ and $R_w(F)$ values of 0·073. The complex (**3**) is isomorphous and isostructural with the corresponding rhenium analogue, $Re_2Br_2(CO)_6P_2Ph_4$ (**2**). The molecular arrangement around the manganese atoms in (**3**) is shown in the Figure. The molecule consists of two hexaco-ordinated manganese atoms surrounded by a set of three *facial* carbonyl groups, two bridging bromides, and a phosphorous atom of the P–P bridge. Relevant structural parameters (average values) are: Mn–Br, 2·526(5) and P–P, 2·322(4) Å; ∠Br–Mn–Br, 85·5(1) and ∠Mn–Br–Mn, 92·5(5)°. The nonbonding Mn ··· Mn distance is 3·661(2) Å [*cf.* 3·743(8) Å for the bromide bridged $Mn_2Br_2(CO)_8$].[8] The folding angle of the molecule, *i.e.* the angle between the normals to the $Mn(CO)_2Br_2$ planes along the Br ··· Br vector is 21·0° [*cf.* 23·4° for the rhenium analogue, essentially zero value for $Mn_2Br_2(CO)_8$].[8] Relevant to this point is the observation that the average P ··· Br contact in (**3**) is 3·32 Å, more than 0·5 Å shorter than the sum of the Br and P van der Waals radii. Apart from $Re_2Br_2(CO)_6P_2Ph_4$ (**2**),[5] no other transition metal complex of P_2R_4 was found to have this geometry, *i.e.* with the diphosphane bridging two co-ordination polyhedra sharing a common edge.

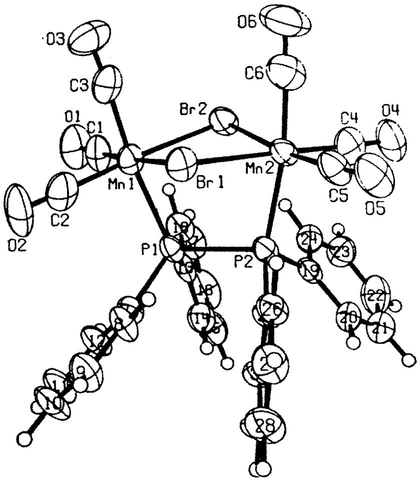


FIGURE. The structure of (**3**).

In view of the relatively drastic conditions used for its synthesis, (**3**) is probably not a kinetically controlled product. Both manganese (I) and rhenium(I) atoms therefore appear to prefer co-ordinative addition to P_2Ph_4 rather than oxidative addition across the P–P bond. This behaviour of substances containing P–P or E–E bonds towards low-valent transition metal complexes is probably the result of a balance between electronic and steric factors more complicated than previously suspected.

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† The atomic co-ordinates for this work are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this Communication.

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