A Homoleptic Arylmanganese(II) Complex: Synthesis and Structure of a Thermally Stable Trinuclear Mesitylmanganse(II) Complex

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The reaction of $MnCl_2$ with mesMgBr (mes = 2,4,6-$C_6H_2Me_3$) gave crystals of the linear trimer mes_6Mn_3 with bridging mesityl groups and the two end Mn atoms three-co-ordinated with a terminal mesityl; the Mn–C bond distances range from 2.10(1) to 2.35(1) Å and the Mn - - - Mn distance is 2.851(3) Å.

The pioneering work in manganese(II) organometallic chemistry has been largely carried out by Wilkinson and co-workers.[1,2] The stabilization of the Mn–C bond, believed to be an unstable unit, was achieved without the help of any ancillary ligand, but using appropriate substituents at the alkyl group preventing β-hydrogen elimination processes.[2] Various polynuclear structures have been identified, in which the alkyl group displays both a bridging 3-centre 2-electron and a terminal bonding mode.[3] There have been few reports so far on the corresponding manganese(II) aryl compounds. The existence of $MnPh_2$[4] has been questioned,[2] while manganese(II) aryl compounds stabilized by a donor atom on the phenyl ring, $[Mn(C_6H_4CH_2NMe_2\text{-}o)_2]$[5] or by a phosphine ligand, $(cy_3P)MnPh_2$[6] (cy = cyclohexyl) have been reported recently without any structural information.

The present report concerns the synthesis and structural determination of a thermally stable homoleptic manganese(II) aryl compound. Manganese(II) chloride was allowed to react with a tetrahydrofuran solution of mesMgBr (mes = 2,4,6-$C_6H_2Me_3$) at −30 °C. From the resulting brown solution magnesium halides were precipitated by adding dioxane. The solution was then evaporated to dryness and the brown residue was recrystallized three times from hot toluene to give deep-maroon crystals of (**1**) (yield *ca.* 50%) [equation (1)].

$$3\ MnCl_2 + 6\ mesMgBr \xrightarrow{-MgBrCl} \underset{(\mathbf{1})}{mes_6Mn_3} \qquad (1)$$

Complex (**1**) is very air sensitive, so microanalytical determination was not possible. It contains one toluene molecule per trimeric unit. The structure was deduced from an *X*-ray analysis.

Crystal Data: $C_{61}H_{74}Mn_3$, triclinic, space group $P\bar{1}$, a = 12.850(3), b = 20.327(4), c = 11.407(3) Å, α = 95.11(2), β = 114.00(2), γ = 98.77(2)°, U = 2652(1) Å^3, Z = 2, D_c = 1.22 g cm^{-3}, $F(000)$ = 1030, Mo-K_α radiation (λ = 0.71069 Å), μ(Mo-K_α) = 7.1 cm^{-1}. The structure was solved by the heavy atom method (Patterson and Fourier syntheses) and refined anisotropically by blocked full matrix least-squares. For 3141 unique observed structure amplitudes [$I > 3\sigma(I)$] collected at room temperature on a Philips PW 1100 diffractometer in the range $5 < 2\theta < 45°$ the current R is 0.062. Most of the hydrogen atoms were located in a difference Fourier map, but owing to the limitations of the version of SHELX[7] used only 32 out of the 74 hydrogen atoms were introduced in the final stage of refinement.†

The structure of (**1**) is given in Figure 1 together with pertinent bond distances and angles. The molecule is a linear trimer with bridging mesityl groups and the two end Mn atoms are tri-co-ordinate, with a terminal mesityl group. Mn(1) has a dis-

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† The atomic co-ordinates for this work are available on request 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.

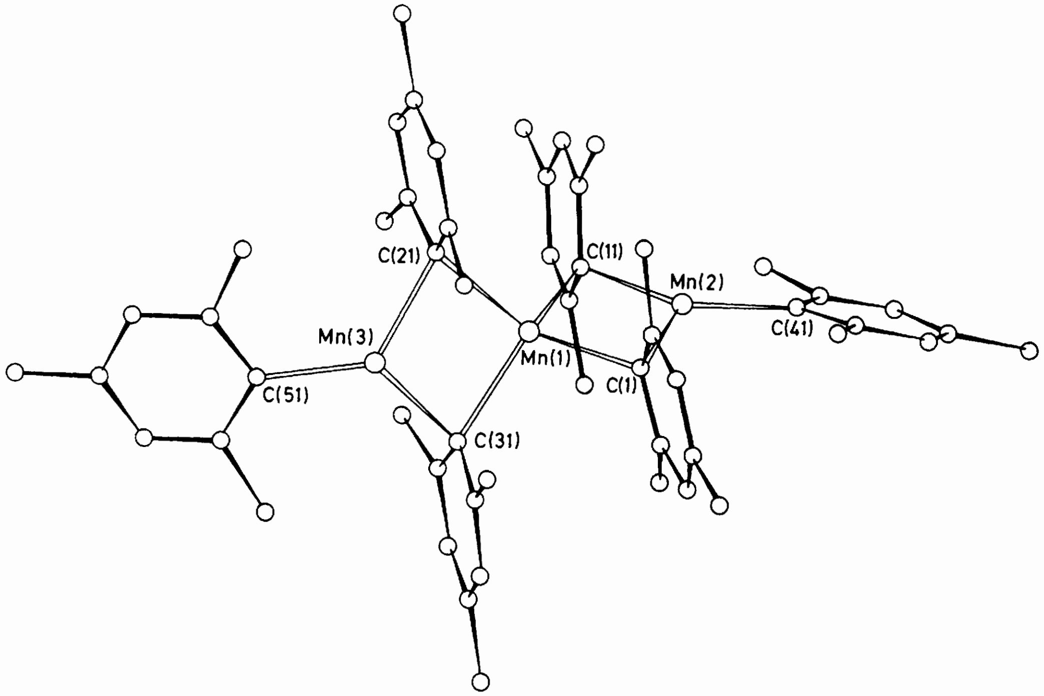

Figure 1. A view of complex (**1**) mes_6Mn_3. Bond distances: Mn(1)–C(1) 2.33(1), Mn(1)–C(11) 2.34(1), Mn(1)–C(21) 2.35(1), Mn(1)–C(31) 2.34(1), Mn(2)–C(11) 2.22(1), Mn(2)–C(41) 2.12(1), Mn(3)–C(21) 2.22(1), Mn(3)–C(31) 2.19(1), Mn(3)–C(51) 2.10(1), Mn(1)–Mn(2) 2.851(3), Mn(1)–Mn(3) 2.851(3) Å. Bond angles: C(21)–Mn(1)–C(31) 98.0(4), C(11)–Mn(1)–C(31) 124.5(4), C(11)–Mn(1)–C(21) 107.3(4), C(1)–Mn(1)–C(31) 105.8(4), C(1)–Mn(1)–C(21) 125.0(11), C(1)–Mn(1)–C(11) 98.6(4), C(11)–Mn(2)–C(41) 130.2 (5), C(1)–Mn(2)–C(41) 122.1(4), C(1)–Mn(2)–C(11) 106.2(4), C(31)–Mn(3)–C(51) 125.8(4), C(21)–Mn(3)–C(51) 125.2(4), C(21)–Mn(3)–C(31) 106.8(4), Mn(2)–Mn(1)–Mn(3) 178.8(1)°.

torted tetrahedral co-ordination, while Mn(2) and Mn(3) have trigonal co-ordination geometry. The deviation from the plane defined by the three carbon donor atoms is 0.155(3) and 0.182(3) Å for Mn(2) and Mn(3), respectively. These two planes form a dihedral angle of 76.7(4)°. The Mn - - - Mn distance [2.851(3) Å] is probably too long for any significant metal–metal bonding beyond that associated with the bridging groups, although the magnetic moment (3.65 μ_B at 299 K) indicates some magnetic interaction.

The mesityl group displays both a bridging and a terminal bonding mode. This, together with the co-ordination number of the manganese atom affects the Mn–C bond distances. The shortest Mn–C bond distances are those involving the terminal mesityl groups [Mn(2)–C(41) 2.12(1) and Mn(3)–C(51) 2.10(1) Å], while the longest are found for Mn(1) binding the bridging mesityl groups [2.33(1)—2.35(1) Å]. Trico-ordinate manganese atoms bond to bridging mesityl groups at shorter distances [2.19(1)—2.22(1) Å]. All these Mn–C bond distances are significantly shorter than those found in the Mn^{II} alkyl complexes [*ca.* 2.7 Å],[3] but are fairly similar to those in $[Mn(CH_2C_6H_4NMe_2\text{-}o)_2]_2$ (2.14—2.38 Å).[5] In alkyl derivatives containing phenyl substituents, weak interactions between the manganese atom and the phenyl group itself or a hydrogen atom from the phenyl group were structurally identified.[2] These interactions do not appear to be present in complex (**1**). All the phenyl rings including the terminal ones are slightly but significantly puckered, with the methyl groups out of the ring plane.

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