The Molecular Structure of Monomeric Base-free Bis(neopentyl)manganese by Gas Electron Diffraction

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The gas electron diffraction pattern of bis(neopentyl)manganese is consistent with a monomer with ∠CMnC = 180° and Mn–C = 210.4(6) pm.

Bis(neopentyl)manganese, $Mn(Me_3CCH_2)_2$, first synthesized by Andersen, Wilkinson, and coworkers, was reported to sublime 'at 100 °C *in vacuo*' and to be very soluble in petroleum.[1] The solid state structure is that of a linear Mn_4 alkyl-bridged tetramer, though details have never been published.[2] We have synthesized $(Me_3CCH_2)_2Mn$ by the method of Andersen *et al.* and recorded the gas electron diffraction data with nozzle and reservoir temperatures of *ca.* 140 °C. At this temperature $(Me_3CCH_2)_2Mn$ is somewhat unstable as evidenced by a black non-volatile residue, but we have nevertheless succeeded in obtaining six consistent and apparently faultless plates covering the scattering range s = 15—152.5 nm^{-1}.

A radial distribution curve obtained by Fourier inversion of the experimental intensities is shown in Figure 1. The curve is very similar to that of monomeric $(Me_3CCH_2)_2Mg$,[3] and entirely consistent with a gas jet containing monomeric species only.

Least-squares refinement of the structure was based on a molecular model of C_2 symmetry (Figure 2) characterized by seven independent parameters (three bond distances, two valence angles, and two torsional angles, see Table 1). These were refined along with eight root-mean-square amplitudes of vibration (l). The best values thus obtained are listed in Table 1. Estimated standard deviations have been multiplied by three to include uncertainty introduced by data correlation and nonrefined parameters.

Table 1. Refined parameters for bis(neopentyl)manganese.

	r_a	l
Bond distances		
Mn–C	210.4(6) pm	9.2(12) pm
C–C	155.2(3) pm	5.0(7) pm
C–H	111.4(6) pm	11.0(6) pm
Nonbonded distances		
Mn- - -C_β	(318 pm)	28(9) pm
Mn- - -C_γ	(331 pm)	17(3) pm
	(383 pm)	21(3) pm
	(448 pm)	14(2) pm
C- - -C	(253 pm)	7.8(7) pm[a]
C_β- - -H	(227 pm)	11.8(7) pm[a]
Valence angles		
∠CMnC	180°[b]	
∠CCC	109.5°[b]	
∠Mn$C_\alpha C_\beta$	120(1)°	
∠$C_\beta C_\gamma$H	116(2)°	
Torsional angles		
$\tau[C_\beta C_\alpha(Mn)\,C_\alpha'C_\beta']$	160(30)°	
$\tau(MnC_\alpha C_\beta C_\gamma)$	156(2)°	

[a] These amplitudes were refined with a constant difference.
[b] Assumed angles.

The vibrational amplitudes obtained for the C–C bond distance and the intra-ligand C–C non-bonded distance are indistinguishable from the corresponding vibrational amplitudes in neopentane,[4] l = 5.1(13) and 7.1(1) pm respectively. This justifies the assumptions made regarding the symmetry of the C_5 framework of the ligand.

The bonding radius of high-spin Mn^{II} is expected to be greater than that of low-spin Mn^{II} and to increase with increasing co-ordination number. Magnetic susceptibility measurements and e.s.r. spectra of the complexes $(PhCMe_2CH_2)_2Mn(PMe_3)_2$ and $(Me_3CCH_2)_2Mn(PMe_3)_2$ in hydrocarbon solution show that they contain five unpaired electrons, *i.e.* high-spin manganese(II).[5] The spin state of a base-free, monomeric dialkylmanganese is unknown, but MnH_2 has a high-spin ground state.[6] The similarity of bond distances in high-spin MnH and MgH, Mn–H = 173.1 and

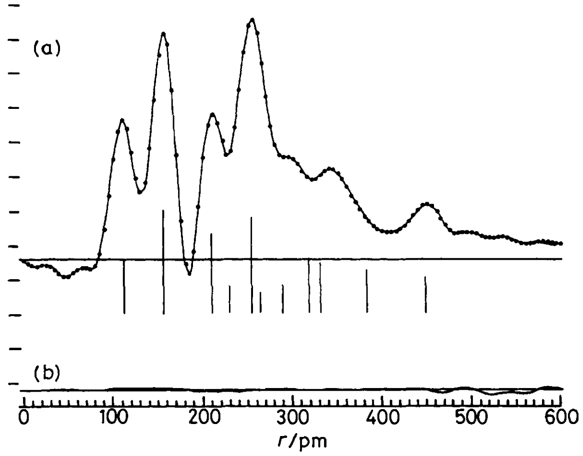

Figure 1. (a) Experimental radial distribution curve for $(Me_3CCH_2)_2Mn$. Artificial damping constant k = 20 pm^2. (b) Difference curve.

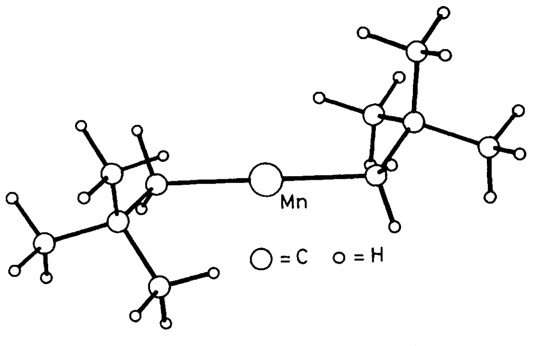

Figure 2. Molecular model of bis(neopentyl)manganese.

Mg–H = 173.0 pm,[7] in high-spin $Mn(\eta^5-C_5H_5)_2$ and $Mg(\eta^5-C_5H_5)_2$, Mn–C = 238.0(6)[8] and Mg–C = 233.9(4) pm,[9] and in $(Me_3CCH_2)_2Mn$ and $(Me_3CCH_2)_2Mg$, Mn–C = 210.3(6) and Mg–C = 212.6(6) pm,[3] also indicate that the dialkyl species is high-spin.

The Mn–C bond distance in monomeric $(Me_3CCH_2)_2Mn$ is significantly shorter than that in the co-ordination compound $(PhMe_2CCH_2)_2Mn(PMe_3)_2$, 214.9(6) pm.[5] Elongation of metal–carbon bonds on co-ordination of electron donors is well known for alkyl derivatives of main group metals.[3] The four Mn–C bond distances in the chelate (high-spin) Mn^{II} complex $Mn(CH_2PMe_2BH_2PMe_2CH_2)_2$ range from 221 to 224 pm.[10] The elongation relative to $(Me_3CCH_2)_2Mn$ may be rationalized by evoking resonance between covalent and dative Mn–C interactions.

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