

## POLYSILANE DERIVATIVES OF THE TRANSITION METALS

### II\*. THE CRYSTAL AND MOLECULAR STRUCTURE OF [TRIS(TRIMETHYLSILYL)SILYL]PENTACARBONYLMANGANESE, (Me<sub>3</sub>Si)<sub>3</sub>SiMn(CO)<sub>5</sub>

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#### SUMMARY

The crystal and molecular structures of [tris(trimethylsilyl)silyl]pentacarbonylmanganese, (Me<sub>3</sub>Si)<sub>3</sub>SiMn(CO)<sub>5</sub>, have been determined from three-dimensional X-ray data obtained by counter methods. The compound crystallizes in space group *P*1̄ of the triclinic system, with two molecules in a unit cell of dimensions: *a* = 9.002(2), *b* = 9.655(2), *c* = 15.639(3) Å,  $\alpha$  = 83.66(1),  $\beta$  = 105.65(1),  $\gamma$  = 114.61(1)°.

The observed and calculated densities are 1.20 ( $\pm 0.03$ ) and 1.23 g·cm<sup>-3</sup> respectively. Full-matrix least-squares refinement of the structure has led to a final value of the conventional *R* factor of 0.059 for the 818 independent reflections having  $F^2 > 3\sigma(F^2)$ .

The coordination geometry about the manganese atom is approximately octahedral and, about the silicon atom bonded to the manganese atom, tetrahedral.

The relative orientations of carbonyl and trimethylsilyl groups, when viewed down the Mn-Si bond, appear consistent with minimization of energy due to non-bonded interactions.

Two of the equatorial carbonyl groups are displaced out of the equatorial plane towards the silicon ligand by 6°. The Si-Mn bond is 2.564(6) Å long and has no multiple character.

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#### INTRODUCTION

The structure of Group IVB derivatives of the transition elements has excited considerable interest for a number of years<sup>2-5</sup>. We have determined the crystal and molecular structures of one such compound [tris(trimethylsilyl)silyl]pentacarbonylmanganese, (Me<sub>3</sub>Si)<sub>3</sub>SiMn(CO)<sub>5</sub>, for a number of reasons. There is a paucity of

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crystallographic data on compounds containing the Si–Mn bond. The structure of only one similar compound,  $\text{Me}_3\text{SiMn}(\text{CO})_5$ , has been reported<sup>6</sup>. Here the shortening of the Si–Mn bond compared with the sum of the covalent radii of the contributing atoms was taken to indicate partial multiple bond character in the metal–metal bond. No structural information was available on compounds containing polysilyl, -germyl or -stannyl ligands. The effect of having a Group IV element other than carbon  $\beta$  to the transition metal atom is also of interest. Furthermore carbonyl derivatives of cobalt and manganese containing hydride<sup>7,8</sup>, halide<sup>9</sup>, Group IVB<sup>6,10–17</sup> or transition metal<sup>11,18–24</sup> ligands exhibit a general displacement of the equatorial carbonyl groups out of the equatorial plane towards the axial non-carbonyl ligands. This observation was originally explained in terms of crystal packing effects<sup>12</sup>, but more recent molecular orbital calculations for a series of Co–Si compounds<sup>25</sup> have led to the postulate of weak bonding interactions between the equatorial carbon atoms and the silicon atom as a cause for the displacement. It was of interest here to determine how the displacement of the equatorial carbonyl groups would be affected by the presence of a bulky  $(\text{Me}_3\text{Si})_3\text{Si}$  ligand in the axial position.

#### EXPERIMENTAL SECTION

Colourless, transparent, irregular shaped crystals of [tris(trimethylsilyl)silyl]-pentacarbonylmanganese,  $(\text{Me}_3\text{Si})_3\text{SiMn}(\text{CO})_5$ , were prepared by a method to be detailed elsewhere<sup>26</sup>, and recrystallized from pentane. Several large crystals were crushed and a wedge-shaped fragment selected for data collection. On the basis of precession photography using Cu- $K\alpha$  X-radiation it was established that the crystals belong to the triclinic system. The success of this analysis has confirmed that the correct space group is  $P\bar{1}$ .

Unit cell dimensions of  $a=9.002(2)$ ,  $b=9.655(2)$ ,  $c=15.639(3)$  Å,  $\alpha=83.66(1)^\circ$ ,  $\beta=105.65(1)^\circ$ ,  $\gamma=114.61(1)^\circ$ , were obtained from a least-squares refinement of the setting angles of 12 reflections accurately centred in a 3.5 mm diameter, circular receiving aperture set 23 cm from the crystal on a Hilger and Watts four circle, computer-controlled diffractometer, [ $\lambda(\text{Mo-}K\alpha)=0.7107$  Å,  $t=23^\circ$ ]. All numbers in this paper refer to this unit cell which can be related to the reduced cell of dimensions  $a=9.66$  Å,  $b=10.10$  Å,  $c=15.64$  Å,  $\alpha=97.75^\circ$ ,  $\beta=96.34^\circ$ ,  $\gamma=125.86^\circ$ , by the matrix 0–10/110/001.

The density calculated for 2 molecules (F.W. 442.65) in the unit cell ( $1.23 \text{ g}\cdot\text{cm}^{-3}$ ) agrees satisfactorily with that measured by flotation and calibrated density gradient tube ( $1.20 \pm 0.03 \text{ g}\cdot\text{cm}^{-3}$ )<sup>27</sup>. Thus no crystallographic symmetry is imposed on the molecule.

The crystal fragment used for data collection was an irregular wedge-shape of maximum dimension 0.34 mm. Its mosaicity was examined by means of open counter  $\omega$ -scans at a take-off angle of  $3^\circ$ ; the widths at half height for intense, low-angle reflections varying<sup>28</sup> from  $0.09^\circ$  to  $0.11^\circ$ . Zirconium filtered Mo- $K\alpha$  X-radiation, and the  $\theta$ - $2\theta$  scan technique, were used to collect the intensities of 1656 reflections in the positive  $h$  hemisphere of reciprocal space for which  $0 < 2\theta \leq 36^\circ$ . A symmetric scan range of  $1.44^\circ$  in  $2\theta$ , centred on the calculated peak position [ $\lambda(\text{Mo-}K\alpha)=0.7107$  Å] was composed of 72 steps of 0.8 seconds duration. Stationary crystal, stationary counter background counts of 15 seconds were measured at each end of the scan range.

No reflections required attenuation to bring them within the linear response range of the scintillation counter, which was located with its 5 mm diameter receiving aperture 23 cm away from the crystal.

During data collection, the intensities of three standard reflections, monitored at regular intervals dropped uniformly to 49% of their original values. These observations were used to place all the intensities on the same relative scale.

An initial correction for background was made and the standard deviation  $\sigma(I)$  of the corrected intensity  $I$  was estimated using the formula.

$$\sigma(I) = [C + 0.25(t_c/t_b)^2 \cdot (B_1 + B_2) + (p \cdot I)^2]^{1/2}$$

where  $C$  is the total integrated peak count obtained in scan time  $t_c$ ;  $B_1$  and  $B_2$  are the background counts, each obtained in time  $t_b$ ;

$$I = C - 0.5(t_c/t_b) \cdot (B_1 + B_2)$$

and, for the initial refinement,  $p$  was given the value 0.05 and is the factor included to avoid overweighting the more intense reflections. The intensities were then corrected for Lorentz and polarisation effects and for absorption ( $\mu \text{ Mo-K}\alpha = 7.94$ ) using Gaussian integration. Minimum and maximum values for transmission coefficients were 0.861 and 0.909 respectively.

Of the 1656 reflections collected, 818 had values of  $F^2$  that were greater than three times their estimated standard deviations and it was these that were used in the final refinement of structure parameters

#### SOLUTION AND REFINEMENT OF STRUCTURE\*

In the full-matrix least-squares refinements the function minimized was  $\Sigma[w \cdot (|F_o| - |F_c|)^2]$  where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure amplitudes respectively, and where the weight  $w$  is  $4F_o^2/\sigma^2(F_o^2)$ .

The agreement factors  $R_1$  and  $R_2$  are defined as

$$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o| \text{ and}$$

$$R_2 = \{ \Sigma[w \cdot (|F_o| - |F_c|)^2] / \Sigma(w \cdot F_o^2) \}^{1/2}$$

The scattering factor tables used for all atoms were calculated using the polynomial constants for HF SCF evaluated by Cromer and Mann<sup>29</sup>. The effects of anomalous dispersion of manganese and silicon atoms were included in  $F_c$ <sup>30</sup> using Cromer's<sup>31</sup> values for  $\Delta f'$  and  $\Delta f''$ .

The positional parameters of the manganese and the four silicon atoms were obtained from an unsharpened three-dimensional Patterson synthesis. Refinement of these coordinates together with isotropic temperature factors for these atoms gave

\* Calculations were carried out at the University of Canterbury using an I.B.M. 360/44 computer with 32K words of core storage and twin 2315 disk drives. The data processing program HILGOUT is based on programs DRED (J. F. Blount) and PICKOUT (R. J. Doedens). Numerical absorption corrections were applied using programs DABS which is a modification of DATAPH (P. Coppens). Mathematical methods are fully described in "Crystallographic Computing" Munksgaard, Copenhagen, 1970. Structure factor calculations and least-square refinements were carried out using program CUCLS and Fourier summations using program FOURIER. These are highly modified versions of the well-known programs ORFLS (W. A. Busing, K. O. Martin and H. A. Levy) and FORDAP (A. Zalkin) respectively.

TABLE 1

FINAL POSITIONAL AND THERMAL PARAMETERS FOR  $[(CH_3)_3Si]_3SiMn(CO)_5$ 

Atom	X	Y	Z	$\beta_{11}^a$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Mn	0.2435(4)	0.3056(3)	0.1225(2)	0.020(1)	0.015(1)	0.0053(2)	0.0096(5)	0.0049(3)	0.0013(2)
Si(4)	0.1146(7)	0.2893(6)	0.2528(3)	0.014(2)	0.012(1)	0.0056(4)	0.0051(9)	0.0036(6)	0.0001(4)
Si(1)	0.1094(8)	0.5252(6)	0.2790(4)	0.025(2)	0.013(1)	0.0070(4)	0.009(1)	0.0063(7)	0.0005(5)
Si(2)	-0.1665(7)	0.1068(6)	0.2306(4)	0.015(2)	0.015(1)	0.0080(4)	0.003(1)	0.0038(6)	0.0002(5)
Si(3)	0.2575(8)	0.2108(7)	0.3872(4)	0.024(2)	0.020(1)	0.0051(4)	0.011(1)	0.0033(6)	0.0017(5)
C(1)	0.345(3)	0.310(2)	0.036(1)	0.032(7)	0.018(4)	0.007(2)	0.015(4)	0.003(3)	0.000(2)
C(2)	0.261(3)	0.131(3)	0.170(1)	0.024(6)	0.021(5)	0.006(1)	0.013(5)	0.002(2)	0.000(2)
C(3)	0.033(3)	0.194(3)	0.052(1)	0.015(6)	0.024(5)	0.004(1)	0.010(5)	-0.003(2)	-0.003(2)
C(4)	0.217(3)	0.478(3)	0.083(1)	0.018(6)	0.011(4)	0.008(2)	0.007(4)	0.004(2)	0.004(2)
C(5)	0.441(3)	0.429(3)	0.198(2)	0.012(7)	0.015(5)	0.009(2)	0.003(5)	0.005(3)	0.000(2)
C(6)	-0.032(3)	0.583(2)	0.179(1)	0.030(6)	0.021(4)	0.007(1)	0.017(4)	0.002(2)	0.006(2)
C(7)	0.332(2)	0.680(2)	0.301(1)	0.014(5)	0.010(3)	0.014(2)	-0.001(3)	0.003(2)	-0.003(2)
C(8)	0.016(3)	0.515(2)	0.376(1)	0.036(7)	0.029(5)	0.007(1)	0.020(5)	0.008(2)	0.001(2)
C(9)	0.497(2)	0.282(2)	0.402(1)	0.010(5)	0.035(5)	0.009(2)	0.008(4)	0.003(2)	0.003(2)
C(10)	0.175(3)	-0.007(2)	0.398(1)	0.044(7)	0.014(4)	0.008(1)	0.012(4)	0.005(3)	0.004(2)
C(11)	0.225(3)	0.283(2)	0.486(1)	0.035(6)	0.033(5)	0.005(1)	0.020(5)	0.007(2)	-0.001(2)
C(12)	-0.322(2)	0.167(2)	0.141(1)	0.009(5)	0.025(5)	0.014(2)	0.010(4)	0.003(2)	0.006(2)
C(13)	-0.238(3)	0.077(2)	0.338(1)	0.027(6)	0.027(5)	0.007(1)	0.010(4)	0.011(2)	0.005(2)
C(14)	-0.188(3)	-0.090(2)	0.197(1)	0.019(6)	0.015(4)	0.012(2)	0.003(4)	0.000(2)	-0.004(2)
O(1)	0.415(2)	0.316(2)	-0.017(1)	0.026(4)	0.034(4)	0.008(1)	0.011(3)	0.008(2)	-0.003(2)
O(2)	0.273(2)	0.023(2)	0.198(1)	0.037(5)	0.023(4)	0.010(1)	0.019(3)	0.008(2)	0.005(2)
O(3)	-0.093(2)	0.121(2)	0.008(1)	0.018(4)	0.027(3)	0.008(1)	0.002(3)	-0.003(2)	-0.004(1)
O(4)	0.202(2)	0.585(2)	0.053(1)	0.045(5)	0.025(3)	0.009(1)	0.024(3)	0.009(2)	0.006(2)
O(5)	0.567(2)	0.508(2)	0.240(1)	0.016(4)	0.024(4)	0.010(1)	0.002(3)	0.001(2)	0.001(2)

<sup>a</sup> The form of the anisotropic ellipsoid is  $\exp[-(\beta_{11} \cdot h^2 + \beta_{22} \cdot k^2 + \beta_{33} \cdot l^2 + 2\beta_{12} \cdot h \cdot k + 2\beta_{13} \cdot h \cdot l + 2\beta_{23} \cdot k \cdot l)]$ .

TABLE 2

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION ( $\text{\AA}$ )<sup>a</sup>

Mn	0.199(7)	0.228(5)	0.278(6)
Si(4)	0.202(11)	0.218(8)	0.258(8)
Si(1)	0.21(1)	0.24(1)	0.30(1)
Si(2)	0.20(1)	0.27(1)	0.30(1)
Si(3)	0.23(1)	0.26(1)	0.29(1)
C(1)	0.22(4)	0.28(3)	0.33(3)
C(2)	0.23(4)	0.25(3)	0.30(3)
C(3)	0.16(5)	0.25(3)	0.32(3)
C(4)	0.18(4)	0.24(4)	0.33(3)
C(5)	0.17(6)	0.26(3)	0.32(4)
C(6)	0.16(4)	0.32(3)	0.34(3)
C(7)	0.17(4)	0.26(3)	0.41(2)
C(8)	0.20(4)	0.30(3)	0.37(3)
C(9)	0.16(5)	0.31(3)	0.40(3)
C(10)	0.20(3)	0.33(3)	0.38(3)
C(11)	0.19(4)	0.31(3)	0.37(3)
C(12)	0.13(6)	0.28(3)	0.44(3)
C(13)	0.15(5)	0.32(3)	0.36(3)
C(14)	0.21(4)	0.29(3)	0.39(3)
O(1)	0.20(3)	0.33(4)	0.39(2)
O(2)	0.23(3)	0.30(2)	0.38(2)
O(3)	0.19(3)	0.36(2)	0.37(2)
O(4)	0.22(3)	0.29(2)	0.41(2)
O(5)	0.22(3)	0.32(2)	0.38(2)

<sup>a</sup> The figures provide an indication of the direction of these principal axes of vibration.

values of 0.312 and 0.415 for  $R_1$  and  $R_2$  respectively. A difference Fourier synthesis revealed the coordinates of all the other non-hydrogen atoms. Using isotropic temperature factors, refinement of this model converged with  $R_1$  and  $R_2$  equal to 0.085 and 0.096 respectively.

Reprocessing the data with  $p=0.09$  led to values for  $R_1$  and  $R_2$  of 0.081 and 0.102 respectively. High values for isotropic temperature factors suggested that anisotropic thermal models would be more appropriate for all atoms and least-squares refinement of this model led to final values for  $R_1$  and  $R_2$  of 0.059 and 0.076 respectively.

A final difference Fourier synthesis showed some peaks that could be assigned to hydrogen atoms but no attempt was made to include these in the model. There were no anomalously high peaks.

The relative weighting scheme appeared satisfactory since  $\Sigma[w \cdot ||F_o| - |F_c||^2]$  showed only slight dependence on  $|F_o|$  and  $\lambda^{-1} \sin \theta$ . The error in an observation of unit weight is 1.17 electrons. Structure factor calculations for the 838 reflections having  $F_o^2 < 3\sigma(F_o^2)$  showed no anomalies of the type  $|F_c| \gg |F_o|$ . There was no evidence for secondary extinction.

The positional and vibrational parameters obtained from the last cycle of refinement are listed in Table 1. Derived root-mean-square amplitudes of vibration for the atoms are listed in Table 2 and some idea of the orientation of the thermal ellipsoids can be obtained from the diagrams. A list of the observed and calculated structure amplitudes for the reflections used in the final refinement can be obtained from the authors.

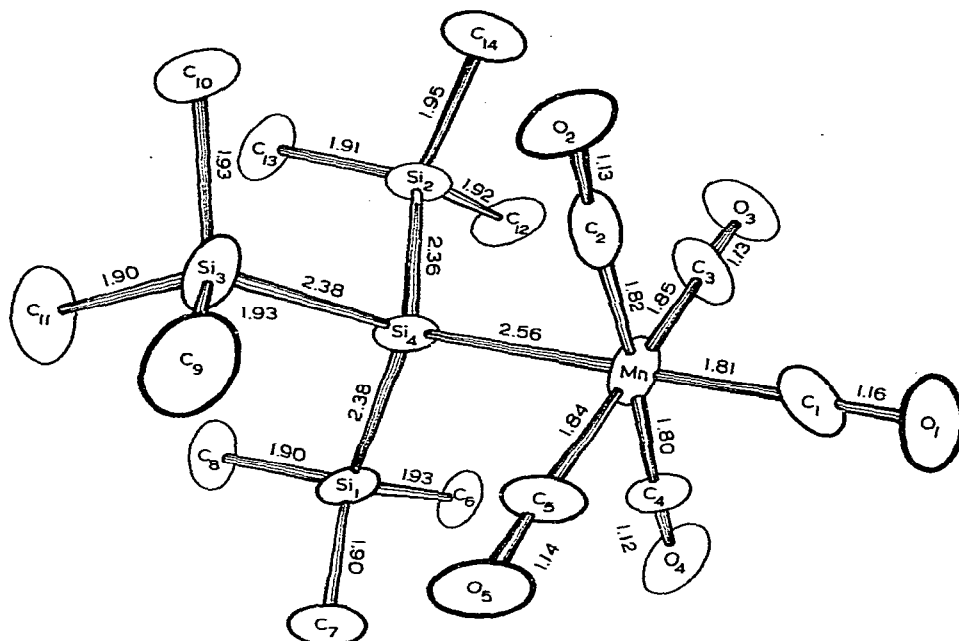


Fig. 1. General view of the  $(\text{Me}_3\text{Si})_3\text{SiMn}(\text{CO})_5$  molecule.

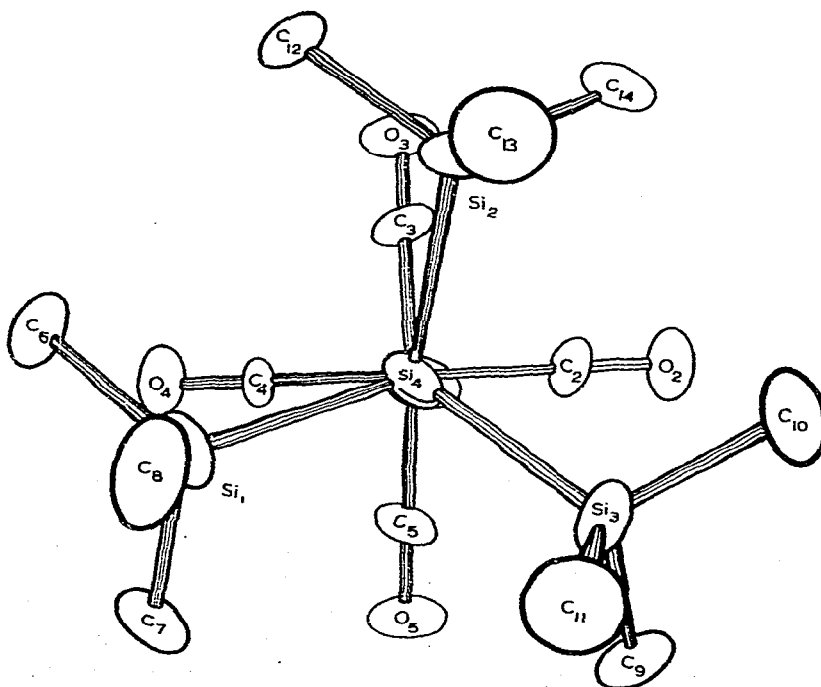


Fig. 2.  $(\text{Me}_3\text{Si})_3\text{SiMn}(\text{CO})_5$  molecule viewed down the Si-Mn axis.

## DISCUSSION

The crystal consists of discrete molecules, the shortest intermolecular, interatomic distance (not involving H atoms) being 3.28 Å. Perspective drawings of the molecule are shown in the Figures; the atom numbering scheme defined in Fig. 1 is used throughout this paper. Selected bonded and non-bonded interatomic distances are given in Table 3 and selected angles of interest in Table 4.

TABLE 3

## SELECTED BONDED AND NON-BONDED DISTANCES (Å)

<i>Bonded distances</i>			
Mn-Si(4)	2.564(6)	Si(4)-Si(1)	2.382(7)
Mn-C(1)	1.81(2)	Si(4)-Si(2)	2.362(8)
Mn-C(2)	1.82(2)	Si(4)-Si(3)	2.378(8)
Mn-C(3)	1.85(2)	Si(1)-C(6)	1.93(2)
Mn-C(4)	1.80(2)	Si(1)-C(7)	1.90(2)
Mn-C(5)	1.84(2)	Si(1)-C(8)	1.90(2)
C(1)-O(1)	1.16(2)	Si(2)-C(12)	1.92(2)
C(2)-O(2)	1.13(2)	Si(2)-C(13)	1.91(2)
C(3)-O(3)	1.13(2)	Si(2)-C(14)	1.95(2)
C(4)-O(4)	1.12(2)	Si(3)-C(9)	1.93(2)
C(5)-O(5)	1.14(2)	Si(3)-C(10)	1.93(2)
		Si(3)-C(11)	1.90(2)
<i>Non-bonded distances (intramolecular)</i>			
Si(4)-C(2)	2.96	C(2)-C(5)	2.67
Si(4)-C(3)	3.18	C(4)-C(5)	2.49
Si(4)-C(4)	3.17	C(2)-C(3)	2.60
Si(4)-C(5)	3.00	C(4)-C(3)	2.57
C(1)-C(2)	2.63	C(2)-C(9)	3.77
C(1)-C(3)	2.63	C(2)-C(14)	3.82
C(1)-C(4)	2.61	C(2)-C(10)	3.83
C(1)-C(5)	2.66	C(3)-C(14)	3.63
C(2)-Si(3)	3.58	C(3)-C(12)	3.73
C(3)-Si(2)	3.56	C(4)-C(7)	3.79
C(4)-Si(1)	3.58	C(4)-C(6)	3.99
C(5)-Si(3)	3.79	C(5)-C(9)	3.34
		C(5)-C(7)	3.63
<i>Shortest intermolecular non-bonded distance</i>			
O(1)-O(1)	3.28		

There is a slightly distorted tetrahedral configuration about Si(4) and the manganese atom is in a distorted octahedral environment. The relative orientations of carbonyl and trimethylsilyl groups, when viewed down the Si-Mn bond (Fig. 2) appear consistent with minimisation of energy due to non-bonded interactions. In particular, the C(2) and C(5) carbonyl groups are bent towards the Si(4) atom, whereas the C(3) and C(4) carbonyl groups are bent towards the axial carbonyl group. Also, the trimethylsilyl groups are rotated about the Si-Si bonds to orientations in which non-bonded interactions with adjacent equatorial carbonyls are minimised.

TABLE 4

## SELECTED ANGLES (DEGREES)

<i>Bonded angles</i>			
Mn-C(1)-O(1)	177(2)	Si(4)-Si(1)-C(6)	111.2(6)
Mn-C(2)-O(2)	178(2)	Si(4)-Si(1)-C(7)	109.6(6)
Mn-C(3)-O(3)	177(2)	Si(4)-Si(1)-C(8)	112.5(6)
Mn-C(4)-O(4)	175(2)	Si(4)-Si(2)-C(12)	112.7(6)
Mn-C(5)-O(5)	176(2)	Si(4)-Si(2)-C(13)	110.0(6)
		Si(4)-Si(2)-C(14)	111.3(6)
Mn-Si(4)-Si(1)	112.0(2)		
Mn-Si(4)-Si(2)	113.2(3)	Si(4)-Si(3)-C(9)	114.2(6)
Mn-Si(4)-Si(3)	112.9(3)	Si(4)-Si(3)-C(10)	112.6(6)
		Si(4)-Si(3)-C(11)	110.1(6)
Si(4)-Mn-C(1)	175.3(7)		
Si(4)-Mn-C(2)	83.3(6)	C(1)-Mn-C(2)	92.8(1)
Si(4)-Mn-C(3)	90.7(6)	C(1)-Mn-C(3)	91.7(1)
Si(4)-Mn-C(4)	91.5(6)	C(1)-Mn-C(4)	92.5(1)
Si(4)-Mn-C(5)	84.2(7)	C(1)-Mn-C(5)	93.6(1)
		C(2)-Mn-C(3)	90.2(1)
Si(1)-Si(4)-Si(2)	106.2(3)	C(2)-Mn-C(4)	174.7(2)
Si(1)-Si(4)-Si(3)	108.4(3)	C(2)-Mn-C(5)	93.8(1)
Si(2)-Si(4)-Si(3)	103.6(3)	C(3)-Mn-C(4)	89.5(1)
		C(3)-Mn-C(5)	173.2(2)
		C(4)-Mn-C(5)	86.0(1)
<i>Dihedral angles<sup>a</sup></i>			
Si(2)-Si(4)-Mn		Si(3)-Si(4)-Mn	
Si(4)-Mn-C(3)	13.6	Si(4)-Mn-C(5)	53.7
Si(1)-Si(4)-Mn		Si(3)-Si(4)-Mn	
Si(4)-Mn-C(4)	16.8	Si(4)-Mn-C(2)	40.9

<sup>a</sup> Angles are between two planes, each defined by three atoms.

### The Si-Mn bond

Attempts to relate the lengths of bonds between a Group IVB element and a transition metal to bond strength, and hence to the degree of multiple bond character, are seriously hampered by the difficulty in obtaining reliable estimates for the covalent radii of transition metal atoms<sup>3,25</sup>. The element manganese is no exception. Estimates for the covalent radius of the manganese atom vary from 1.46 Å<sup>32</sup> to 1.30 Å<sup>33</sup> although more recent<sup>9</sup> determinations favour values of  $\approx 1.38$  Å. Values of the covalent radius of silicon are generally obtained by halving the Si-Si distance in the appropriate polysilane. In this way, fairly close agreement on the silicon radius is obtained using polysilanes with different silicon substituents<sup>25</sup>. Thus halving the Si-Si bond length obtained for  $(\text{Me}_3\text{Si})_4\text{Si}^{34}$  gives a silicon radius of 1.18 Å which together with the value of 1.38 Å for the manganese radius provides an estimated Si-Mn single bond length of 2.56 Å. Our results show that the M-Mn bond in  $(\text{Me}_3\text{Si})_3\text{SiMn}(\text{CO})_5$  is unique in being approximately equal to the predicted M-Mn single bond length (M = Si, Ge, Sn). This suggests that electronic effects resulting from  $(d-d)\pi$  bonding in the Si-Mn bond, or bonding interactions between the equatorial carbon atoms and the axial silicon atom, which should have the effect of shortening the Si-Mn bond are outweighed by the necessity to minimise steric repulsions involving the bulky  $(\text{Me}_3\text{Si})_3\text{Si}$  ligand.



There is a small but significant deviation from a tetrahedral environment about Si(4). The mean Mn–Si(4)–Si bond angle is  $112.7^\circ$  and the mean Si–Si(4)–Si bond angle is  $106.1^\circ$ . The average bonded Si–Si distance is  $2.374(5) \text{ \AA}$  and this is significantly longer than the average Si–Si bond length of  $2.352(3) \text{ \AA}$  found in  $(\text{Me}_3\text{Si})_4\text{Si}^{34}$ . All this is expected both on account of the greater crowding of atoms in this region of the former molecule, and because of the relatively unsymmetrical arrangement of the equatorial carbonyl groups with respect to the  $(\text{Me}_3\text{Si})_3\text{Si}$  fragment. No Si–C bond deviates significantly from the mean value of  $1.92 \text{ \AA}$ , which agrees with the mean value of  $1.89 \text{ \AA}$  found in  $(\text{Me}_3\text{Si})_4\text{Si}$ . There is, therefore, no evidence of increased conjugative electron withdrawal due to the presence of Si atoms  $\beta$  to the transition metal atom in this molecule, although such an effect has been noted in other organopolysilane systems<sup>35,36</sup>.

The displacement of C(3) and C(4) towards C(1), and C(2) and C(5) towards Si(4) and Si(3) has been explained in terms of simple steric effects. The location of C(1) off the Si(4)–Mn vector but equidistant from C(2), C(3), C(4) and C(5) also confirms the importance of steric effects in determining the detailed stereochemistry even in unsymmetric complexes. It is therefore unnecessary to invoke a bonding interaction between the axial silicon and equatorial carbon atoms to explain the observed conformation, although the Si(4)–C(eq) non-bonded distances are such that an interaction of this type cannot be definitely precluded. There is no significant difference between the various Mn–C bond lengths, nor the various C–O bond lengths of the carbonyl groups. Such differences have been suggested possible in situations where the transition metal to silicon bond has some multiple character<sup>15</sup>.

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