Crystal and Molecular Structure of Tetracarbonyl(trimethylsilyl)(triphenyl-phosphine)manganese(I)

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The crystal structure of the title compound has been determined from *X*-ray diffractometer data by the heavy-atom method. Crystals are triclinic, space group $P\bar{1}$, with a = 1251.0(2), b = 1150.3(2), c = 1011.5(2) pm, α = 117.62(2), β = 101.72(2), γ = 91.90(2)°, and Z = 2. The structure was refined by block-diagonal least-squares to R 0·070 for 1 537 observed reflections.

The co-ordination geometry about manganese is approximately octahedral, and about silicon and phosphorus tetrahedral. The silyl and phosphine ligands are mutually *trans*. Si–Mn [245.3(4) pm] is significantly shorter than expected. The carbonyl groups are displaced 6° out of the equatorial plane towards the silyl ligand.

INCREASING emphasis is being placed on the importance of *X*-ray structural determinations in the study of compounds containing covalent bonds between transition metals and main-group metals or metalloids.[1-3] Interest has centred not only on elucidating the gross structures of these molecules, but also on obtaining evidence from bond-length [1] and bond-angle [4] data in support of current theories on the nature of the metal–metal bonds. Our interest in the electronic and steric consequences of silyl substitution at transition-metal centres [5,6] led to the present study of tetracarbonyl(trimethylsilyl)(triphenylphosphine)manganese(I). In this molecule, the length of the Si–Mn bond should reflect the replacement of a carbonyl group *trans* to silicon with the weaker π-acceptor triphenylphosphine ligand. We also wished to determine the effect of substitution by the bulky phosphine ligand on the co-ordination geometry at manganese.

EXPERIMENTAL

Preparation.—Irregular crystals were prepared by hydrogen elimination between Me_3SiH and $[Mn_2(CO)_8(PPh_3)_2]$,[6] and crystallised from hexane.

Crystal Data.—$C_{25}H_{24}MnO_4PSi$, M = 502.5, Triclinic, a = 1251.0(2), b = 1150.3(2), c = 1011.5(2) pm, α = 117.62(2), β = 101.72(2), γ = 91.90(2)°, $U = 1.249 \times 10^9$ pm^3, D_m = 1.33(5) g cm^{-3}, Z = 2, D_c = 1.34 g cm^{-3}, $F(000)$ = 520. Mo-K_α radiation, λ = 71.07 pm, μ(Mo-K_α) = 6.94 cm^{-1}. Space-group was confirmed as $P\bar{1}$ by the subsequent successful analysis.

Preliminary space-group and unit-cell data were obtained from precession photographs by use of Cu-K_α radiation, (λ = 154.18 pm) and all quantitative *X*-ray data (Zr-filtered Mo-K_α radiation) from a Hilger and Watts four-circle diffractometer controlled by a PDP 8F computer. The wedge-shaped crystal used for data collection had maximum and minimum dimensions 0.43 and 0.15 mm. To minimise decomposition by *X*-radiation it was mounted with random orientation with Araldite inside a glass capillary. Unit-cell parameters were obtained by least-squares refinement of the setting angles of twelve reflections accurately centred in a 5 mm diameter receiving aperture by an adaptation of the method of ref. 7.

The crystal mosaicity was examined by means of open-counter ω-scans at a take-off angle of 3°; the widths at half-height for intense, low-angle reflections ranged from 0.10 to 0.12°. Intensity data were collected in the bisecting mode ($\omega = \theta$). The θ—2θ scan technique was used with a symmetric 2θ scan range of 1.20° centred on the calculated peak position and was composed of 30 steps of 1 s. Stationary-crystal—stationary-background counts of 7.5 s were recorded at each end of the scan. Crystal stability was confirmed by the constancy of three reference reflections whose intensities were regularly monitored.

A standard deviation $\sigma(I)$ was assigned to each measured intensity according to the expression: $\sigma(I) = [c + (t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{\frac{1}{2}}$, where c is the scan count, B_1 and B_2 are the background counts, t_b and t_c are scan and background times respectively, and p is an empirical coefficient [8] of the nett count I which was given the value 0.05 for the initial refinement. Of the total of 3 169 reflections recorded in the hemisphere of reciprocal space where h is positive and $0 < 2\theta < 44°$, 1 537 reflections having intensities $I > 3\sigma(I)$ were considered observed. Data were not corrected for absorption as trial calculations had shown the transmission coefficients to lie within the narrow range 0.92—0.90.

Solution and Refinement of the Structure.—The positions of the manganese and phosphorus atoms were obtained from a three-dimensional Patterson synthesis. A series of difference-Fourier maps and least-squares cycles led to the location of all other non-hydrogen atoms. From this point the phenyl rings were treated as rigid regular hexagons each with 7 associated parameters, 3 to define position, 3 to define orientation, and one overall isotropic temperature factor. All other atoms were assigned individual isotropic temperature factors.

The block-diagonal least-squares refinements were based on the structure factor F and the function minimised was $\Sigma w(|F_o| - |F_c|)^2$, where the weight, w, was $4F_o^2/[\sigma(F_o)^2]^2$. Scattering-factor curves used for all atoms were taken from ref. 9, values for manganese, phosphorus, and silicon being corrected for the effects of anomalous dispersion ($\Delta f'$, $\Delta f''$).[10] Refinement of this model converged with R 0.122

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[1] C. S. Cundy, B. M. Kingston, and M. F. Lappert, *Adv. Organometallic Chem.*, 1973, **11**, 253.

[2] F. Glockling and S. R. Stobart, in *M.T.P. Internat. Rev. Sci.*, 1972, **6**, p. 63.

[3] E. H. Brooks and R. J. Cross, *Organometallic Chem. Rev.*, 1970, **6**, 227.

[4] A. D. Berry, E. R. Corey, A. P. Hagen, A. G. MacDiarmid, F. E. Saalfeld, and B. B. Wayland, *J. Amer. Chem. Soc.*, 1970, **92**, 1940.

[5] B. K. Nicholson, W. T. Robinson, and J. Simpson, *J. Organometallic Chem.*, 1973, **47**, 403.

[6] B. K. Nicholson and J. Simpson, *J. Organometallic Chem.*, 1974, **72**, 211.

[7] W. R. Busing, in 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, p. 319.

[8] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **7**, 197.

[9] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[10] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

and R' 0.132 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}},\ R = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]\}$.

Reprocessing the data with $p = 0.095$ led to R 0.120 and R' 0.144. For final refinement, the thermal vibration of all the non-group atoms was described by the six-parameter ellipsoid model. Hydrogen atoms were not included in the calculations. At convergence, R was 0.070, and R' 0.093 for the 1 537 reflections for which $|F_o|^2 \geqslant 3\sigma(|F_o|^2)$. The highest residual peak in a final electron-density difference map was 0.7×10^{-6} e pm^{-3} compared with 2.7×10^{-6} e pm^{-3} for the last carbon atom located by this technique.

TABLE 1

Final positional and thermal parameters * for non-group atoms

Atom	x	y	z	$10^8\beta_{11}$	$10^8\beta_{22}$	$10^8\beta_{33}$	$10^8\beta_{12}$	$10^8\beta_{13}$	$10^8\beta_{23}$
Mn	0.227 5(2)	−0.028 4(2)	−0.153 2(2)	48(2)	65(2)	83(3)	13(2)	15(2)	34(2)
P	0.208 9(3)	0.162 3(3)	−0.172 5(4)	51(3)	74(4)	86(6)	9(3)	14(3)	38(4)
Si	0.242 7(3)	−0.222 4(4)	−0.113 0(5)	79(4)	93(5)	159(8)	24(4)	31(5)	79(5)
O(1)	0.357 4(9)	−0.155(1)	−0.385(1)	110(10)	150(10)	160(20)	40(10)	80(10)	60(10)
O(2)	0.034 8(8)	−0.218 8(9)	−0.391(1)	76(9)	110(10)	180(20)	−17(9)	−40(10)	70(10)
O(3)	0.113 4(7)	0.048 9(9)	0.099(1)	81(9)	160(10)	130(20)	14(9)	70(10)	60(10)
O(4)	0.434 0(7)	0.100 2(9)	0.097(1)	69(9)	140(10)	140(20)	1(9)	−0(10)	40(10)
C(1)	0.309(1)	−0.104(1)	−0.294(2)	60(10)	70(20)	100(30)	0(10)	10(20)	30(20)
C(2)	0.108(1)	−0.143(1)	−0.305(2)	60(10)	70(10)	130(20)	10(10)	20(10)	50(20)
C(3)	0.154(1)	0.021(1)	0.002(1)	50(10)	80(20)	100(20)	10(20)	20(10)	50(20)
C(4)	0.355(1)	0.050(1)	−0.004(1)	60(10)	110(20)	110(20)	30(10)	40(10)	60(20)
C(5)	0.344(1)	−0.184(2)	0.075(2)	90(20)	190(20)	220(30)	0(20)	−20(20)	160(20)
C(6)	0.105(1)	−0.296(1)	−0.110(2)	90(10)	110(20)	210(30)	−30(10)	−20(20)	90(20)
C(7)	0.290(2)	−0.365(1)	−0.270(2)	240(20)	90(20)	240(30)	110(20)	140(20)	70(20)

* The β values are the coefficients in the anisotropic temperature factor expression:

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

TABLE 2

Final positional and thermal parameters * for group atoms

Atom	x	y	z
Ring (1)			
C(11)	0.275 7(8)	0.311 8(8)	0.011 6(8)
C(12)	0.373 0(9)	0.386(1)	0.030 7(9)
C(13)	0.425 9(9)	0.490(1)	0.175(1)
C(14)	0.381 5(8)	0.519 3(8)	0.300 9(8)
C(15)	0.284 2(9)	0.445(1)	0.281 8(9)
C(16)	0.231 3(9)	0.341(1)	0.137(1)
Ring (2)			
C(21)	0.069 6(5)	0.205 0(8)	−0.215(1)
C(22)	0.057 4(6)	0.337 1(7)	−0.168 6(9)
C(23)	−0.046 6(7)	0.370 9(6)	−0.203(1)
C(24)	−0.138 2(5)	0.272 5(8)	−0.283 7(9)
C(25)	−0.125 4(6)	0.140 3(7)	−0.329 7(9)
C(26)	−0.022 0(7)	0.106 6(6)	−0.295(1)
Ring (3)			
C(31)	0.272 3(7)	0.178 6(9)	−0.313 6(9)
C(32)	0.378 7(9)	0.148(1)	−0.318(1)
C(33)	0.428 2(6)	0.157(1)	−0.426(1)
C(34)	0.371 2(7)	0.196 0(9)	−0.528 1(9)
C(35)	0.264 8(9)	0.226(1)	−0.523(1)
C(36)	0.215 3(6)	0.218(1)	−0.416(1)

* B values ($\times 10^4$), parameters in the isotropic temperature-factor expression $\exp[-B(\sin\theta)^2/\lambda^2]$, represent overall values for each ring, and are: ring (1) 4.5, ring (2) 3.6, and ring (3) 4.1 pm^2.

The minimised function showed little systematic dependence on either F_o or $\sin\theta$, and a calculation of the structure factors for the reflections having $F_o{}^2 < 3\sigma(F_o{}^2)$ revealed no anomalies. Final positional and thermal parameters for those atoms refined as individuals are listed in Table 1 and those for the group atoms (phenyl rings) are listed in Table 2. Root-mean square amplitudes of vibration for the atoms refined anisotropically and final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21611 (4 pp., 1 microfiche).†

All calculations were carried out on a Burroughs 6712 computer. The program HILGOUT to process diffractometer paper-tape output is based on programs DRED (J. F. Blount) and PICKOUT (R. J. Doedens). Structure-factor calculations and least-squares refinements were carried out by use of program CUCLS and Fourier summations with program FOURIER, highly modified versions of the well-known programs ORFLS (W. A. Busing, K. O. Martin, and H. A. Levy) and FORDAP (A. Zalkin) respectively. Interatomic distances and angles and thermal vibration analysis were obtained from program ORFFE, also by Busing, Martin, and Levy. DANTEP, a modification of ORTEP by C. K. Johnson, was used for interatomic distance and angle calculations and for production of structure diagrams on an incremental plotter.

RESULTS AND DISCUSSION

The crystal consists of discrete molecules, the shortest interatomic distance (not involving H atoms) being 295 pm. The atom numbering scheme is defined in Figure 1. Figure 2 shows the molecule viewed down the Si–Mn–P axis, and Figure 3 the arrangement of molecules in the unit cell. Table 3 lists selected bonded and non-bonded interatomic distances, Table 4 selected angles, and Table 5 dihedral angles.

The overall geometry of the molecule shows the co-ordination of the Si and P atoms to be roughly tetrahedral. The silyl and phosphine ligands occupy *trans*-positions in the distorted Mn octahedron, confirming earlier predictions of the molecular geometry from i.r. spectroscopic data.[6] The view down the Si–Mn–P axis shows the Si–C and P–C bonds to be partially eclipsed. Deviation from a totally eclipsed conformation is however far more marked in this molecule than for the Sn–C and P–C bonds in [$(Ph_3Sn)Mn(CO)_4(PPh_3)$].[11] The C(2)

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† See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[11] R. F. Bryan, *J. Chem. Soc.* (*A*), 1967, 172.

and C(3) carbonyl groups are staggered relative to the Si–C and P–C bonds, with the Me_3Si group adopting a conformation in which the Si–C(6) bond (in projection) approximately bisects the C(2)–Mn–C(3) angle. The remaining equatorial carbonyl groups are partially eclipsed by both the methyl and phenyl substituents on the axial ligands.

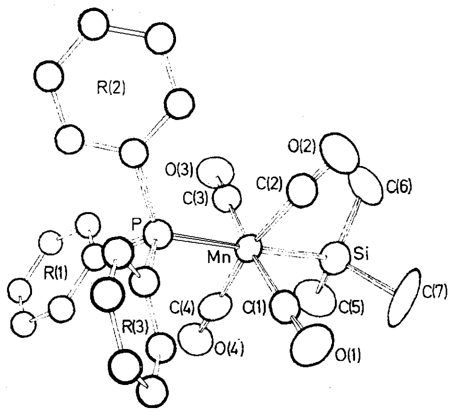

FIGURE 1 General view of the molecule

The Si–Mn *and* Mn–P *Bonds*.—The expected single-bond length of a Si–Mn bond calculated from the sum of covalent radii of the contributing Si (117 pm) * and Mn (138 pm) † atoms is 255 pm.[5] The present Si–Mn internuclear separation is 245.3(4) pm, establishing the presence of a covalent bond between the two atoms which is considerably shorter than the single-bond value. This distance is also significantly shorter than the corresponding distance in [$(Me_3Si)Mn(CO)_5$] [249.8(5) pm], [14] or the sterically crowded [$(Me_3Si)_3SiMn(CO)_5$][256.4(6) pm].[5] An immediate advantage of these latter comparisons is that the observed changes in bond length with substitution of the Mn atom do not rely on a knowledge of the covalent radius of manganese.

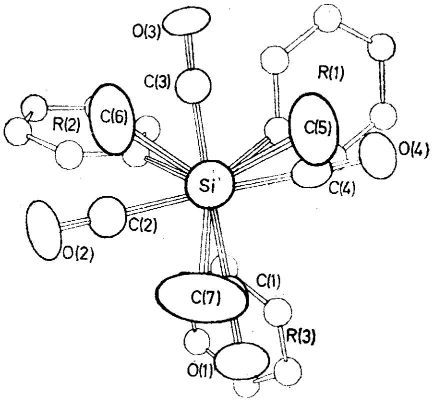

FIGURE 2 The molecule viewed down the Si–Mn–P axis

The decrease in length of the Si–Mn bond in [(Me_3Si)-$Mn(CO)_4PPh_3$] compared to that in molecules in which the silicon substituent is *trans* to a carbonyl group can most readily be attributed to the differing σ-donor/π-acceptor characteristics of the triphenylphosphine and carbonyl ligands, it being generally accepted that the former is the better σ-donor but poorer π-acceptor.[15] Phosphine substitution would therefore result in an overall increase in electron density at manganese. More particularly, electron density would increase in the orbitals of π-symmetry whence it could be used in a d_π–d_π bonding interaction across the Si–Mn bond. This situation is reflected in the decreased Si–Mn length. A similar effect was observed for phosphine substitution *trans* to a Sn–Mn bond.[11]

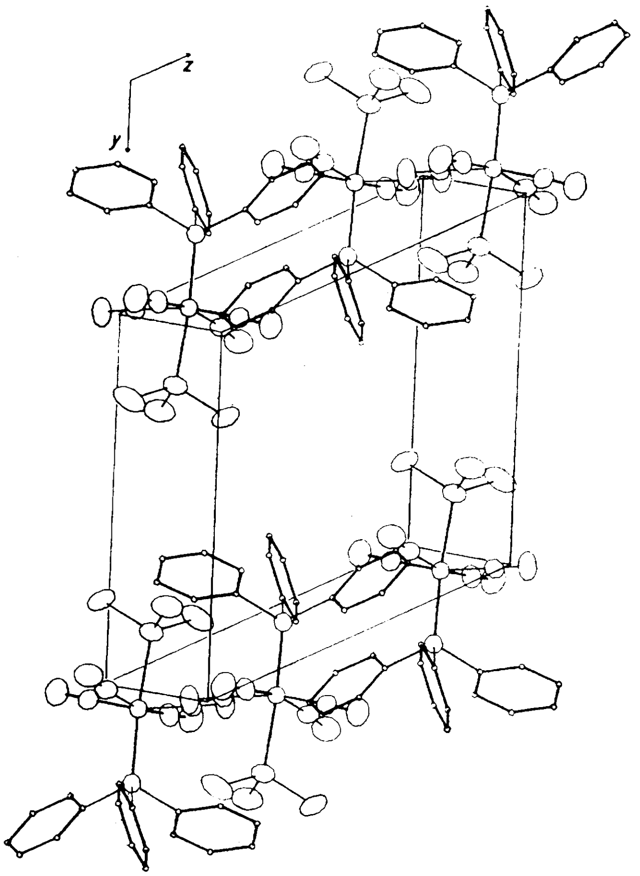

FIGURE 3 The arrangement of atoms in the unit cell as viewed down the *a* axis

Evidence for the involvement of the Si and P atoms in a mutually dependent bonding interaction also comes from the Mn–P distance [230.6(4) pm], which is longer by some 4—5 pm than the corresponding distances in a

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* Obtained by halving the Si–Si distance in $Me_3Si{\cdot}SiMe_3$.[12]

† For a discussion of the problems associated with assigning covalent radii to the transition elements see refs. 5 and 13.

[12] L. O. Brockway and N. R. Davidson, *J. Amer. Chem. Soc.*, 1941, **63**, 3287.

[13] N. C. Baird, *Progr. Inorg. Chem.*, 1968, **9**, 1.

[14] R. S. Hamilton and E. R. Corey, Abs. Inorg. Div. 156th Nat. Meeting Amer. Chem. Soc., Atlantic City, N.J., Sept. 1968, No. 025; R. S. Hamilton and E. R. Corey, personal communication.

[15] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Wiley, New York, 1972, p. 719—721.

variety of other phosphine-substituted manganese carbonyls in which the phosphine substituent is *trans* to species with little or no π-acceptor tendencies (Table 6). In the absence of π-effects, this observation would be difficult to explain. The characteristic *trans*-influence of the Ph_3P ligand[16] should lead to polarisation of the electron density at manganese *via* a σ-interaction, in a sense that would tend to weaken the Si–Mn bond. Unusually long bonds between platinum and substituents, X, *trans* to phosphine ligands are well known, and have been taken as indicative of weakened Pt–X bonding.[16,17] However, i.r.,[18,19] n.m.r.,[20] and crystallographic[21] studies on Si–Pt compounds reveal that silyl substituents R_3Si have an even greater *trans*-influence than phosphines. These observations have been rationalised in terms of increased inductive electron release by the silyl ligand rather than the combination of inductive and mesomeric effects which would be required if the metal–silicon bond were to have a significant d_π–d_π component.

TABLE 3

Selected bonded and non-bonded distances (pm)

Bonded distances			
Mn–Si	245.3(4)	C(3)–O(3)	111.8(8)
Mn–P	230.6(4)	C(4)–O(4)	116.6(9)
Mn–C(1)	182.4(2)	Si–C(5)	190.3(4)
Mn–C(2)	184.3(2)	Si–C(6)	190.6(4)
Mn–C(3)	185.1(2)	Si–C(7)	189.6(4)
Mn–C(4)	181.6(2)		
		P–C(11)	185.1(3)
C(1)–O(1)	114.3(9)	P–C(21)	184.7(3)
C(2)–O(2)	112.9(9)	P–C(31)	184.4(3)
Non-bonded intramolecular distances			
P···C(1)	313	C(1)···C(2)	252
P···C(2)	322	C(1)···C(4)	255
P···C(3)	305	C(2)···C(3)	270
P···C(4)	297	C(3)···C(4)	254
		C(1)···C(31)	338
Si···C(1)	296	C(1)···C(32)	312
Si···C(2)	281	C(2)···C(21)	374
Si···C(3)	285	C(2)···C(26)	331
Si···C(4)	298	C(3)···C(11)	358
		C(3)···C(16)	330
C(1)···C(7)	313	C(3)···C(21)	373
C(2)···C(6)	320	C(3)···C(26)	388
C(2)···C(7)	357	C(4)···C(11)	315
		C(4)···C(12)	371
C(3)···C(5)	361	C(4)···C(16)	353
C(3)···C(6)	327	C(4)···C(32)	389
C(4)···C(5)	315		
Shortest intermolecular non-bonded distance			
O(3)···O(3)	295		

TABLE 4

Selected angles (°)

Mn–C(1)–O(1)	177.3(5)	P–Mn–Si	175.3(2)
Mn–C(2)–O(2)	174.3(4)	P–Mn–C(1)	98.1(1)
Mn–C(3)–O(3)	176.7(5)	P–Mn–C(2)	101.3(1)
Mn–C(4)–O(4)	176.5(5)	P–Mn–C(3)	93.8(1)
		P–Mn–C(4)	91.6(1)
Mn–Si–C(5)	113.0(2)		
Mn–Si–C(6)	112.5(2)	Si–Mn–C(1)	86.4(1)
Mn–Si–C(7)	113.6(2)	Si–Mn–C(2)	80.2(1)
		Si–Mn–C(3)	81.7(1)
Mn–P–C(11)	111.3(2)	Si–Mn–C(4)	87.2(1)
Mn–P–C(21)	119.4(2)		
Mn–P–C(31)	116.3(2)	C(1)–Mn–C(2)	86.7(1)
		C(1)–Mn–C(3)	167.8(1)
C(5)–Si–C(6)	106.7(2)	C(1)–Mn–C(4)	89.1(1)
C(5)–Si–C(7)	105.8(2)	C(2)–Mn–C(3)	93.9(1)
C(6)–Si–C(7)	104.7(2)	C(2)–Mn–C(4)	166.9(1)
		C(3)–Mn–C(4)	87.8(1)
C(11)–P–C(21)	101.4(2)		
C(11)–P–C(31)	103.6(2)		
C(21)–P–C(31)	102.8(2)		

In the present molecule, the Si–Mn and Mn–P distances indicate clearly that competition for *trans*-influence favours silicon. The order of inductive electron release for the series Me_3M (M = Si, Ge, or Sn) has been established as $Me_3Sn > Me_3Ge > Me_3Si$ from a comparison of rates of cleavage of M–C bonds.[22] A similar order results from analyses of the carbonyl stretching force constants in $[(Me_3M)Mn(CO)_5]$ with subsequent calculation of the Graham $\Delta\sigma$ and $\Delta\pi$ parameters.[6,23] The Me_3Si group is therefore unlikely to prove the exceptional σ-donor required if inductive effects alone are to explain its unusually high *trans*-influence. If, however, this σ-donation is enhanced by a synergic back-bonding interaction between manganese and silicon, an explanation is found for both the short Si–Mn bond and the length of the corresponding Mn–P distance.

TABLE 5

Dihedral angles (°) *

C(5)–Si–Mn Si–Mn–C(4)	16.1	C(11)–P–Mn P–Mn–C(4)	27.8
C(7)–Si–Mn Si–Mn–C(1)	15.2	C(31)–P–Mn P–Mn–C(1)	1.3
C(6)–Si–Mn Si–Mn–C(2)	46.2	C(21)–P–Mn P–Mn–C(2)	37.2
C(6)–Si–Mn Si–Mn–C(3)	48.8	C(21)–P–Mn P–Mn–C(3)	57.5
C(5)–Si–Mn–P C(11)–P–Mn–Si	11.7	C(7)–Si–Mn–P C(31)–P–Mn–Si	14.6
C(6)–Si–Mn–P C(21)–P–Mn–Si	7.9		

* Between two planes, each defined by either three or four atoms.

In this context note that Mn–P in $[(Ph_3Sn)Mn(CO)_4(PPh_3)]$[11] [226(2) pm] is significantly shorter than the present value. Comparison of the Graham $\Delta\sigma$ parameters for Me_3Si[6] and Ph_3Sn[23] indicates an approximately equal propensity towards inductive electron release, suggesting that factors other than σ-donation determine the observed differences in Mn–P bond length. Unusually long Mn–P bonds have also been observed in molecules such as $[ClMn(CO)_4(PPh_3)]$,[24] where the

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[16] A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1966, 1707; L. M. Venanzi, *Chem. in Britain*, 1968, **4**, 162; S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, 1968, **90**, 6669.

[17] F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, 1962, **4**, 381.

[18] J. Chatt, C. Eaborn, S. D. Ibekwe, and P. N. Kapoor, *J. Chem. Soc.* (*A*), 1970, 1343.

[19] F. Glockling and K. A. Hooton, *J. Chem. Soc.* (*A*), 1967, 1066.

[20] B. T. Heaton and A. Pidcock, *J. Organometallic Chem.*, 1968, **14**, 235.

[21] R. McWeeney, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, 1969, **47**, 20.

[22] R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1964, **2**, 154.

[23] W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 315.

[24] H. Vahrenkamp, *Chem. Ber.*, 1971, **104**, 449.

phosphorus atom is *trans* to the π-acceptor CO ligand (Table 6).

TABLE 6

Structural data for phosphine-substituted manganese carbonyls

Complex	Mn–P/pm	Ligands or ligand moieties *trans* to P
$[Mn_2(CO)_8(PMePh_2)_2]$ [a]	223 *	$Mn(CO)_4{\cdot}PMePh_2$
$[Mn_2(CO)_9PMe_2Ph]$ [b]	223.9 *	$Mn(CO)_5$
$[Mn_2(CO)_8(PEt_3)_2]$ [c]	224.7(7)	$Mn(CO)_4(PEt_3)$
$[HMn(CO)_3(PMePh_2)_2]$ [d]	225.5 *	$PMePh_2$
$[(Me_3Sn)Mn(CO)_4(PPh_3)]$ [e]	226.7(19)	$SnMe_3$
$[(Ph_3P)AuMn(CO)_4P(OPh)_3]$ [f]	227(2)	$Au{\cdot}P(OPh)_3$
$[(Me_3Si)Mn(CO)_4(PPh_3)]$ [g]	230.6(4)	$SiMe_3$
$[ClMn(CO)_4(PPh_3)]$ [h]	239.8(4)	CO

* Estimated standard deviations not quoted.

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Further evidence in support of the conclusion that σ-donation is not solely responsible for the observed *trans*-influence comes from a re-examination of data for compounds of the type *trans*-$[PtCl(MR_3)(PR_3)_2]$ (M = Si or Sn; R = alkyl or aryl).[18,19,25] In these systems, a decrease in ν(Pt–Cl) is found to be characteristic of powerful *trans*-influence by the Group IV substituents. Purely on the basis of inductive electron release, ν(Pt–Cl) should be lower for tin than for silyl ligands whereas in fact the opposite trend is found (Table 7). Comparisons of Pt–M (M = Si and Sn) and Pt–Cl bond lengths, together with analysis of $^{195}Pt–^{31}P$ coupling constants for the tin-substituted compounds, would further clarify these trends.

TABLE 7

Pt–Cl Stretching frequencies for *trans*-$[PtCl(MR_3)(PR^1_3)_2]$ complexes (M = Si and Sn)

Complex	ν(Pt–Cl)/cm^{-1}
$[PtCl(SiMe_3)(PEt_3)_2]$	238 [a]
$[PtCl(SiPh_3)(PMe_2Ph)_2]$	239 [b]
$[PtCl(SiMe_2Ph)(PMe_2Ph)_2]$	242 [b]
$[PtCl(SnEt_3)(PPh_3)_2]$	272 [b]
$[PtCl(SnMe_3)(PPh_3)_2]$	278 [c], 296 [d]
$[PtCl(SnPh_3)(PPh_3)_2]$	298 [e]

[a] Ref. 19. [b] Ref. 18. [c] D. J. Cardin and M. F. Lappert, *Chem. Comm.*, 1966, 506. [d] Ref. 25. [e] M. C. Baird, *J. Inorg. Nuclear Chem.*, 1967, **29**, 367.

Configuration about Manganese.—The mean Mn–C (183.3 pm) and corresponding C–O distances (113.9 pm) do not differ appreciably from values obtained in other silyl-substituted manganese carbonyls.[5,14] The mean Mn–C–O angle (176.2°) indicates a marked departure from linearity, a feature of the majority of metal carbonyl systems. All the carbonyl ligands are displaced (mean 6°) out of the equatorial plane towards silicon. While individual displacements, as measured by Si–Mn–CO or P–Mn–CO angles, will be affected by the non-linearity of the Si–Mn–P axis, the overall bending towards the apical silicon must be regarded as significant.

Examination of non-bonded distances (Table 3) reveals contacts of similar magnitude between the carbonyl ligands and carbon atoms from both the methyl groups and the phenyl rings. This suggests that minimisation of non-bonded interactions between the carbonyl groups and substituents on phosphorus and silicon figures prominently in determining the extent of carbonyl displacement. Despite this the closest non-bonded contacts involving carbonyl groups are between carbonyl groups themselves, with mean C(eq) ··· C(eq) 257 pm. In addition, the Si ··· C(eq) non-bonded distances (mean 290 pm) are significantly less than the corresponding P ··· C(eq) contacts (mean 309 pm). The possibility of a bonding interaction between the silicon atom and the carbonyl groups contributing to the strength of the Si–Mn bond and providing at least some of the driving force for carbonyl displacement towards the apical silicon, cannot therefore be ruled out. Such interactions have previously been invoked to explain the ' umbrella ' bending of co-ordinated carbonyl groups in a variety of Group IV substituted transition-metal complexes.[4] Similar schemes have also been suggested to account for analogous displacements in halogeno-[26] and polynuclear[27] metal carbonyl derivatives.

Configurations about Silicon and Phosphorus.—Significant deviations from exact tetrahedral environments are evidenced by the angles around both these atoms: mean Mn–Si–C 113.0° and mean C–Si–C 105.7°. Similar deviations are observed in a number of R_3M (M = Si or Sn; R = alkyl or aryl) derivatives of manganese carbonyls[5,11,14,28] and are not unique to *trans*-phosphine substitution. Departure from ideal tetrahedral geometry is more marked about phosphorus: mean Mn–P–C 115.5°, and mean C–P–C 102.6°. In systems where there is a significant contraction of the metal–phosphorus bond, such effects have been attributed to an increase in the *p* orbital character in the P–C bonds.[29] In this molecule however steric interactions, between the phenyl substituents on phosphorus and the equatorial carbonyl ligands, are a more likely cause of the observed distortions.

The average Si–C bonded distance (190.2 pm) shows a slight increase over values for Me_4Si (1.89 pm)[30] and Me_3SiH (187.3 pm).[31] It is however shorter than Si–C in $[(Me_3Si)Mn(CO)_5]$ (192 pm).[14] The P–C bond lengths do not differ significantly, but the mean (184.7 pm) is appreciably greater than that (182.3 pm) for free triphenylphosphine.[32] Such discrepancies are to be ex-

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pected in view of the close contacts between carbonyl carbon atoms and the methyl and phenyl groups.

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