Structural Characterization of Di-μ-diphenylsilyl-bis(tetracarbonylmanganese), $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$. Stereochemical Analysis of an Organosilyl-Bridged Dimer Containing a Metal–Metal Interaction

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Abstract: A structural characterization by single-crystal X-ray diffraction of the Jetz–Graham complex, $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$, has ascertained its molecular geometry and has provided hitherto unreported structural information concerning the stereochemistry of a nonhydrogen-bridged manganese dimer containing a spin-coupling metal–metal interaction. $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ crystallizes with two discrete dimeric molecules in a monoclinic unit cell of centrosymmetric symmetry $A2/m$ and of dimensions $a = 11.788$ Å, $b = 10.480$ Å, $c = 13.744$ Å, and $\beta = 117.37°$; the calculated and observed densities are 1.538 and 1.54 (1) g cm^{-3}, respectively. A full-matrix, least-squares refinement with anisotropic thermal parameters for all nonhydrogen atoms gave final discrepancy factors of $R_1 = 4.0\%$ and $R_2 = 4.5\%$ for the 879 independent, diffractometry-collected data with $I \geq 2\sigma(I)$. The dimer may be described as a dioctahedral structure formed by two *cis*-$Mn(CO)_4$ moieties being symmetrically linked to each other by two bridging diphenylsilyl ligands. The crystallographically imposed site symmetry of C_{2h}-$2/m$, which has the twofold axis passing through the two manganese atoms and the mirror plane passing through the two silicon atoms and bisecting the Mn–Mn bond, not only requires the resulting Mn_2Si_2 rhombus to be exactly planar but also requires one of the two phenyl rings attached to each silicon atom to be randomly disordered between two crystal orientations. The $Mn_2(CO)_8Si_2$ fragment approximately conforms to D_{2h} symmetry which is reduced to molecular C_2 symmetry by inclusion of the phenyl rings. The formation of an electron pair Mn–Mn bond is strongly evidenced by a severe distortion of the Mn_2Si_2 ring as shown from the sharply acute bridging Mn–Si–Mn bond angles of 73.4 (1)° and by a Mn–Mn distance (2.871 (2) Å) comparable to that in $Mn_2(CO)_{10}$ (2.923 (3) Å). A detailed comparison of the structural features of $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ with those of related complexes (with and without similar metal–metal interactions) is made together with a discussion of the Mn–Mn and Mn–Si bonding.

Structural investigations by X-ray analysis have now established that a large number and variety of organo–transition metal dimers may be stabilized either by metal–metal interactions *per se* or by one or more bridging ligands both with and without metal–metal interactions. Dinuclear manganese complexes have been ascertained by X-ray diffraction studies to exist either *via* direct metal–metal interactions only, as in $Mn_2(CO)_{10}$[1] and its axially substituted derivatives $Mn_2(CO)_8(PR_3)_2$ (where R = F,[2] C_2H_5[3]), or *via* bridging ligands but without metal–metal interactions, as in $Mn_2(CO)_8(\mu\text{-}Br)_2$.[4] The only previously reported X-ray study of a ligand-bridged manganese dimer which contains a metal–metal interaction is that by Doedens, Robinson, and Ibers[5] of $Mn_2(CO)_8(\mu\text{-}H)(\mu\text{-}P(C_6H_5)_2)$. The metal–metal interaction in this molecule, which contains a "bent" symmetrical Mn–H–Mn linkage, may be formulated either as a superposition of a metal–metal σ bond and a "resonating" M–H σ bond[5] or alternatively in terms of a three-center electron pair representation (formally arising from a protonation of the electron pair metal–metal bond) which involves metal–metal bonding character.

Within the last 5 years numerous organosilicon groups covalently bonded to transition metals have been prepared and extensively studied, especially with regard to a comparison of their physical-chemical properties with those of the germanium and tin analogs.[6–11] Structural studies of molecular compounds with *terminal* organosilyl ligands include $Co(CO)_3(SiX_3)$ (where X = H,[12] F,[13] Cl[14]), $Fe(h^5\text{-}C_5H_5)(CO)(SiCl_3)_2$,[15] $Rh(H)(SiCl_3)(Cl)(P(C_6H_5)_3)_2 \cdot xSiHCl_3$,[16] $Mn(CO)_5(Si(CH_3)_3)$,[17] $Mn(h^5\text{-}C_5H_5)(CO)_2HSi(C_6H_5)_3$,[18] and $Zr(h^5\text{-}C_5H_5)_2(Cl)(Si(C_6H_5)_3)$.[19] However, silicon–tran-

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sition metal chemistry appears to differ notably from gemanium- and tin-transition metal chemistry in the relative paucity of polynuclear metal species containing heterocyclic rings with silicon ligands coordinated to two or more transition metals.[6-10,20-30] Furthermore, no structural data on any organometallic complexes containing silicon heterocyclically linked to more than one transition metal are as yet reported (to our knowledge)[31,32] in contrast to the many structurally proven examples illustrating the diverse nature of germanium- and tin-bridged heterocyclic ring systems—*e.g.*, $Fe_2(CO)_6(\mu\text{-}Ge(CH_3)_2)_3$,[33] $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}Ge(C_6H_5)_2)_2$,[34] $Co_2(CO)_6(\mu\text{-}CO)[\mu\text{-}Ge(C_6H_5)(Co(CO)_4)]$,[35] $Co_2(h^5\text{-}C_5H_5)_2(\mu\text{-}CO)_2(\text{-}GeCl_2\text{-}Fe(CO)_4\text{-}GeCl_2\text{-})$,[36-38] $Ru_3(CO)_9(\mu\text{-}Ge(CH_3)_2)_3$,[39,40] $[Fe_2(CO)_8(\mu\text{-}Sn(CH_3)_2)]_2Sn$,[41] and $[Fe_2(CO)_8]_2Sn$.[42]

The preparation of $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ by Jetz and Graham,[43] who from infrared and nmr data postulated a D_{2h} silyl-bridged structure with a Mn–Mn bond, afforded the opportunity to examine the detailed structural characteristics of a nonhydrogen-bridged manganese dimer containing an electron pair metal–metal interaction.[44,45] It was of particular interest to us to determine the degree of influence of the Mn–Mn interaction upon the molecular geometry, as evidenced from the Mn–Mn distance as well as from the acuteness of the angles subtended at the silicon atoms. Another purpose of this study was to gather stereochemical information in order to compare a M_2Si_2 ring system deformed by a M–M interaction with other four-

(20) The linkage of a $Si(C_6H_5)_2$ ligand to each of two rhenium atoms through a bridging hydrogen atom was postulated by Hoyano, Elder, and Graham[21] from their synthesis and structural characterization of a diphenylsilane-rhenium carbonyl complex, $Re_2(CO)_8(H)_2(Si(C_6H_5)_2)$. Its approximate C_{2v} geometry, which may be described in terms of each of the two hydrogen atoms of a $H\text{-}Si(C_6H_5)_2\text{-}H$ fragment formally replacing one of the four equatorial carbonyls on each rhenium atom of a (Re–Re)-bonded D_{4h}-eclipsed conformation of $Re_2(CO)_{10}$,[22] was determined from an X-ray crystallographic analysis (which located the nonhydrogen atoms) and combined with nmr and infrared spectroscopic data (which reasonably inferred the hydrogen positions). The correspondence of the observed Si–Re distances of 2.544 (9) Å to an expected covalent bond length provides evidence of extensive Si–Re bonding character in the initially presumed three-center electron pair Si–H–Re bond due to direct overlap of the Si and Re orbitals with each other as well as with hydrogen 1s orbitals. On the basis of Raman spectral measurements of $Re_2(CO)_8(H)_2(Si(C_6H_5)_2)$ and related rhenium complexes indicating simple Re–H stretching vibrations in the terminal region coupled with the fact that the formation of the postulated Si–H bond produced no significant change in the geometry of the Re_2Si_2 bridging system (as demonstrated by a comparison of the structures of $Re_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ and $Re_2(CO)_6(H)_4(Si(C_2H_5)_2)_2$), it was later proposed[23,24] that the Si–H interaction is probably the result of steric crowding and is likely very weak. Subsequently, Bennett and Simpson[23] reported the crystal and molecular structure of $W_2(CO)_8(H)_2(Si(C_2H_5)_2)_2$ and ascribed the dissimilar W–Si bond lengths in terms of hydrogen insertion into the longer Si–W bonds to give a truly three-center, electron-pair Si–H–W bond.

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(22) In this connection, Gapotchenko, *et al.*,[25] recently reported from an analysis of electron diffraction data that $Re_2(CO)_{10}$ possesses an eclipsed D_{4h} configuration in the gaseous state. Furthermore, they asserted[25] that the X-ray diffraction study[26] of crystalline $Re_2(CO)_{10}$ established only the Re–Re bond length (and hence not the molecular geometry), and they also stated[25] that, in contrast to $Mn_2(CO)_{10}$[1] and $Tc_2(CO)_{10}$[27] which possess a D_{4d} conformation, $Re_2(CO)_{10}$ has an eclipsed D_{4h} geometry. We wish to point out that their interpretation of the crystal and molecular structure of $Re_2(CO)_{10}$ being different from those of $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ is completely unfounded, and moreover we believe from the previously stated stereochemical considerations[28] based on the structures of related dimers (together with the Re–Re bond length of 3.04 Å determined from the electron diffraction investigation[25]) that $Re_2(CO)_{10}$ maintains the D_{4d} staggered geometry in the gaseous state (in contradistinction to their analysis of the radial distribution function). It is particularly noteworthy that electron diffraction studies of $Mn_2(CO)_{10}$ showed the molecule to remain unaltered in the gaseous state in a staggered D_{4d} conformation.[29] Not only is the crystal structure of $Re_2(CO)_{10}$ isomorphous with those of $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ (as revealed from the unit cells having analogous lattice parameters and the identical space group) but also a detailed comparison of the corresponding intensity data of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ substantiated the essentially identical nature of their structures.[1,26] For $Re_2(CO)_{10}$, intensity data of the three principal reciprocal lattice zones were used to locate unambiguously all the carbonyl ligands in the unit cell by means of Fourier projections.[26] The overall structure of $Re_2(CO)_{10}$ was subsequently confirmed by a least-squares refinement of three-dimensional data for $Mn_2(CO)_{10}$.[1]

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(31) Subsequent to our X-ray analysis of $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ presented here, an X-ray diffraction study (as yet unpublished) of the corresponding rhenium analog, $Re_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$, was carried out by Bennett and Haas[32] who found the rhenium complex to be isostructural with the manganese one.

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membered bridged systems (with and without metal–metal interactions)[46] in related dimers which have been structurally characterized.

Experimental Section

Unit Cell and Space Group. Yellow diamond-shaped crystals of $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ were generously supplied by Dr. W. Jetz and Professor W. A. G. Graham (Department of Chemistry, University of Alberta). A single crystal of dimensions 0.30 × 0.29 × 0.155 mm along the [210], [$\bar{2}$10], and [001] directions, respectively, was chosen for the X-ray investigations. Preliminary Weissenberg and precession photographs exhibited the monoclinic Laue symmetry of C_{2h}-$2/m$. Systematic absences for $\{hkl\}$ of $k + l = 2n + 1$ indicated the possible space groups to be $A2$, Am, or $A2/m$. The centrosymmetric space group $A2/m$ was shown to be the correct choice from the successful refinement of the determined structure (*vide infra*). After optical and X-ray alignment of the crystal on a Datex-controlled full-circle General Electric diffractometer,[47] 17 reflections were carefully centered with Mo Kα radiation (λ 0.7107 Å). The angular coordinates (2θ, ϕ, χ) obtained for these reflections were least-squares refined[48] to give lattice parameters of a = 11.7879 (15) Å, b = 10.4795 (19) Å, c = 13.7442 (22) Å, and β = 117.367 (6)°.[49] The volume of the unit cell is 1507.9 Å^3. The experimental density of 1.54 (1) g cm^{-3} measured by the flotation method is in accord with the calculated density of 1.538 g cm^{-3} for Z = 2.

Intensity data were collected on the diffractometer which was equipped with a scintillation counter and pulse height analyzer adjusted to admit 90% of the Zr-filtered Mo Kα radiation. All independent reflections with $2\theta \leq 45.0°$ were measured *via* the θ–2θ scan technique. A scan speed of 2 deg/min was employed with scan widths of 2.5° for reflections with $2\theta \leq 9.0°$ and 2.0° for reflections with $9.0° < 2\theta \leq 45.0°$. Background counts of 15.0 sec duration were made by stationary crystal–stationary counter measurements on each side of the peak. Four octants (*viz.*, hkl and $\bar{h}kl$, which correspond to the asymmetric unit, and the twofold-related $\bar{h}k\bar{l}$ and $hk\bar{l}$) of the intensity-weighted reciprocal lattice were sampled, so that after merging, the resultant intensity of each independent reflection was a weighted average of the intensity measurements of symmetry-equivalent reflections. Four standard reflections, measured at regular intervals of every 100 reflections in order to monitor crystal alignment and decay (as well as instrumental stability), showed no significant deviations during the entire data collection. For each reflection the intensity and its standard deviation were calculated according to the formulas $I = S - B\cdot(T/t)$ and $\sigma(I) = [S + B(T/t)^2 + (\rho I)^2]^{1/2}$, where I is the net integrated intensity, S the total scan count measured for time T, B the total background count for time t, and ρ the conventional ignorance factor arbitrarily assigned a value of 0.04. The criterion used for a reflection to be considered as statistically observed was that $I \geq 2\sigma(I)$. All data were corrected for Lorentz–polarization effects and reduced to $|F_o|$'s.

Since the transmission factors (based on a linear absorption coefficient of 10.7 cm^{-1} for Mo Kα radiation) ranged from 0.76 to 0.90, absorption corrections were applied[50] to the individual $|F_o|$'s and the data then merged[51] into a basic asymmetric unit consisting of 879 independent observed reflections. No corrections for extinction were made.

Solution of the Structure. An interpretation of a three-dimensional Patterson map[52] provided probable positions for the four Mn and four Si atoms in the unit cell. On the basis of a trial model of $A2/m$ symmetry, with each Mn atom located on a twofold axis and each Si atom located on a mirror plane, successive Fourier syntheses[52] revealed initial coordinates for all nonhydrogen atoms in the unit cell. For this model, one of the two phenyl rings attached to each Si was required to lie on a mirror plane with the other ring bisected by the mirror plane. However, several cycles of isotropic least-squares[53,54] refinement of the nonhydrogen atoms under $A2/m$ symmetry resulted in inordinately high thermal parameters for several of the phenyl carbon atoms. Although a Fourier difference synthesis based on these isotropic parameters did not reveal the nature of the crystallographic disorder, there were indications from the shapes and contours of the observed peaks that the $2/m$ crystallographic symmetry requirements placed improper constraints (in agreement with the large isotropic thermal parameters) on the positional parameters of the in-plane phenyl ring. In order to account for these deviations, a trial model of $A2$ crystallographic symmetry was then adopted. Least-squares refinement of this model with isotropic thermal parameters resulted in discrepancy factors R_1 = 13.3% and R_2 = 16.7%. Continued refinement with anisotropic thermal coefficients utilized for the Mn, Si, and carbonyl atoms reduced R_1 to 5.7% and R_2 to 6.6% at convergence. However, an examination of chemically equivalent parameters revealed excessively large variations which could not be easily explained. These differences were reflected in the variance–covariance matrix, where very high correlations were found among the y parameters of several atoms which were apparently related by a crystallographic mirror plane through the two silicon atoms. This indicated that the probable space group is $A2/m$. Full-matrix least-squares refinement with anisotropically varying thermal parameters for all nonhydrogen atoms resulted in R_1 = 5.0% and R_2 = 5.8% for a model of $A2/m$ symmetry in which one phenyl ring was constrained to lie on the crystallographic mirror plane while the other phenyl ring was bisected by the mirror plane. A Fourier difference synthesis phased on the parameters of the Mn, Si, carbonyl atoms, and carbon atoms of the latter phenyl ring correctly revealed the nature of the crystallographic disorder. The phenyl ring which was assumed to lie on the mirror plane was actually slightly canted with respect to it with the two orientations (related by the mirror plane) each having an occupancy factor of 0.5. Actually, one of the six phenyl carbon atoms in this disordered ring was assumed to lie on the mirror plane (with an individual occupancy factor of 1.0), while the other ten carbon and hydrogen atoms are each half-weighted. Full-matrix refinement of this model with anisotropic temperature coefficients for all nonhydrogen atoms resulted in final residuals of R_1 = 4.0% and R_2 = 4.5%.

Throughout these refinements the positions of the hydrogen atoms were idealized on the basis of the locations of the carbon atoms.[55,56] The isotropic temperature coefficient of each hydrogen atom was fixed at 3.0 Å^2. The final "goodness-of-fit" parameter was 0.83 which indicates a slight over-estimation of the standard deviation of an observation of unit weight.

The scattering factors used in the structure factor calculations were those of Hanson, *et al.*[57] Real and imaginary corrections for anomalous dispersion (*viz.*, $\Delta f'$ = 0.4, $\Delta f''$ = 0.9 for Mn; $\Delta f'$ = 0.1, $\Delta f''$ = 0.1 for Si)[58] were included in the final cycles of the least-squares refinement. Although the results of the final refinement are significant at the 0.5% level,[59] the corresponding parameters of the Mn_2Si_2 rhombus are identical within 2σ for all three refinements (*i.e.*, the model based on $A2$ symmetry, the crystal-ordered model of $A2/m$ symmetry, and the preferred crystal-disordered model of $A2/m$ symmetry).

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(56) The C–H used distance of 1.00 Å is slightly shorter than the internuclear distance of 1.085 Å obtained from electron diffraction studies. This is in deference to the fact that X-rays are scattered by electron density and not by atomic nuclei.

(57) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

(58) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 214.

(59) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

The atomic coordinates from the output of the last least-squares cycle of the crystal-disordered model are presented in Table I.[60]

Table I. Final Positional and Thermal Parameters for $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$[a]

A. Positional Parameters

Atom	x	y	z
Mn	0	0.13696 (9)	0
Si	0.16022 (14)	0	0.13206 (12)
C(1)	0.1004 (3)	0.1405 (4)	−0.0713 (3)
O(1)	0.1615 (3)	0.1513 (3)	−0.1148 (3)
C(2)	0.1015 (3)	0.2518 (5)	0.1001 (3)
O(2)	0.1605 (3)	0.3270 (3)	0.1625 (2)
C(1-1)[b]	0.1945 (6)	0.0173 (75)	0.2807 (5)
C(1-2)	0.3159 (6)	0.0489 (9)	0.3600 (6)
C(1-3)	0.3452 (7)	0.0543 (10)	0.4691 (6)
C(1-4)	0.2574 (7)	0.0264 (27)	0.5031 (6)
C(1-5)	0.1352 (6)	0	0.4264 (5)
C(1-6)	0.1041 (5)	0.0008 (32)	0.3166 (5)
C(2-1)	0.3231 (5)	0	0.1377 (4)
C(2-2)	0.3865 (4)	0.1115 (5)	0.1406 (4)
C(2-3)	0.5086 (4)	0.1111 (5)	0.1485 (5)
C(2-4)	0.5674 (5)	0	0.1516 (6)
H(1-2)[c]	0.3829	0.0670	0.3363
H(1-3)	0.4338	0.0769	0.5253
H(1-4)	0.2804	0.0273	0.5828
H(1-5)	0.0691	−0.0180	0.4511
H(1-6)	0.0141	−0.0162	0.2603
H(2-2)	0.3420	0.1938	0.1378
H(2-3)	0.5541	0.1929	0.1514
H(2-4)	0.6546	0	0.1567

B. Thermal Parameters[d]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Mn[e]	67 (1)	88 (1)	34 (1)	0	27 (1)	0
Si[e]	63 (1)	104 (2)	34 (1)	0	24 (1)	0
C(1)	88 (4)	100 (5)	51 (3)	−20 (4)	37 (3)	−12 (3)
O(1)	155 (4)	153 (4)	99 (3)	−31 (4)	98 (3)	−17 (3)
C(2)	77 (3)	116 (5)	48 (3)	5 (4)	33 (3)	−8 (4)
O(2)	125 (3)	135 (4)	70 (2)	−18 (3)	38 (2)	−37 (3)
C(1-1)	83 (5)	71 (62)	34 (4)	−5 (11)	27 (4)	3 (9)
C(1-2)	85 (7)	159 (16)	48 (5)	−13 (8)	33 (5)	−11 (7)
C(1-3)	85 (7)	192 (17)	47 (6)	−1 (9)	14 (5)	−21 (8)
C(1-4)	118 (8)	153 (45)	42 (5)	24 (13)	27 (5)	−9 (9)
C(1-5)	125 (7)	121 (8)	52 (5)	0	51 (5)	0
C(1-6)	84 (6)	143 (10)	46 (5)	−19 (30)	27 (5)	−59 (18)
C(2-1)	70 (5)	112 (7)	46 (4)	0	28 (4)	0
C(2-2)	93 (4)	108 (6)	139 (5)	−15 (4)	62 (4)	−44 (5)
C(2-3)	86 (4)	137 (6)	170 (6)	−32 (5)	75 (4)	−22 (6)
C(2-4)	66 (6)	182 (11)	89 (6)	0	41 (5)	0

[a] In this and subsequent tables the estimated standard deviations of the last significant figures are given in parentheses. [b] The carbon and hydrogen atoms of phenyl ring 1 (except C(1-5)) correspond to a crystallographic disorder in which each atom has an occupancy factor of 0.5. C(1-5) which lies on the crystallographic mirror plane has unit occupancy. [c] The positional parameters for each hydrogen atom were idealized by use of MIRAGE[55] to calculate a vector from the centroid of each ring through the respective carbon atom to give a C–H distance of 1.00 Å. [d] The anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. All hydrogen atoms were refined with an isotropic thermal parameter of 3.0 Å². [e] For those atoms located on the crystallographic twofold axis or on the crystallographic mirror plane, β_{12} and β_{23} are required by symmetry to be zero.

Table II gives interatomic distances and bond angles with estimated standard deviations calculated from the variance–covariance matrix,[61] while Table III supplies some least-squares planes of interest.[62]

(60) Observed and calculated structure factors for $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-783. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Table II. Interatomic Distances (Å) and Angles (deg) for $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$

A. Bond Distances[a]

Mn(1)–Mn(2)	2.871 (2)	Mn–Si	2.402 (2)
Mn–C(1)	1.852 (4)	C(1)–O(1)	1.134 (4)
Mn–C(2)	1.805 (5)	C(2)–O(2)	1.137 (5)
Si–C(1-1)	1.900 (5)	C(1-4)–C(1-5)	1.366 (11)
Si–C(2-1)	1.885 (10)	C(1-5)–C(1-6)	1.377 (14)
	1.892 (av)	C(1-6)–C(1-1)	1.380 (10)
C(1-1)–C(1-2)	1.382 (21)	C(2-1)–C(2-2)	1.377 (5)
C(1-2)–C(1-3)	1.376 (10)	C(2-2)–C(2-3)	1.394 (5)
C(1-3)–C(1-4)	1.350 (12)	C(2-3)–C(2-4)	1.345 (6)
			1.372 (av)

B. Nonbonding Intramolecular Distances

Si···Si	3.852 (3)	C(1)···C(4)	2.944 (9)
		C(1)···C(2)	2.623 (6)
Si···C(1)	2.944 (4)	C(1)···C(2′)	2.513 (6)
Si···C(2)	2.712 (5)	C(2)···C(2′)	2.692 (7)

C. Bond Angles

Mn(1)–Si–Mn(2)	73.39 (6)	Mn(1)–Mn(2)–C(1)	91.1 (1)
Si–Mn–Si′	106.61 (6)	Mn(1)–Mn(2)–C(2)	131.8 (1)
Mn–C(1)–O(1)	175.4 (4)	C(1)–Mn–C(2)	91.7 (2)
Mn–C(2)–O(2)	176.8 (3)	C(1)–Mn–C(1′)	177.7 (3)
Mn(1)–Si–C(1-1)	117.6 (1)	C(1)–Mn–C(2′)	86.8 (2)
Mn(1)–Si–C(2-1)	117.4 (17)	C(2)–Mn–C(2′)	96.4 (3)
Mn(2)–Si–C(2-1)	125.0 (16)		
C(1-1)–Si–C(2-1)	104.2 (3)		
Si–C(1-1)–C(1-2)	120.2 (8)	Si–C(2-1)–C(2-2)	122.0 (3)
Si–C(1-1)–C(1-6)	123.8 (13)		
C(1-6)–C(1-1)–C(1-2)	116.0 (8)		
C(1-1)–C(1-2)–C(1-3)	121.3 (8)		
C(1-2)–C(1-3)–C(1-4)	121.3 (7)		
C(1-3)–C(1-4)–C(1-5)	118.8 (6)		
C(1-4)–C(1-5)–C(1-6)	119.9 (7)		
C(1-5)–C(1-6)–C(1-1)	122.2 (6)		
C(2-6)–C(2-1)–C(2-2)	116.0 (5)		
C(2-1)–C(2-2)–C(2-3)	121.9 (4)		
C(2-2)–C(2-3)–C(2-4)	120.2 (5)		
C(2-3)–C(2-4)–C(2-5)	119.9 (5)		

D. Selected Nonbonding Intermolecular Distances[b]

H(1-2)···H(1-3)^{I}	2.126	C(1-2)···C(1-3)^{I}	3.585 (9)
H(1-3)···H(1-3)^{I}	1.980	C(1-3)···C(1-3)^{I}	3.344 (15)
O(1)···O(2)^{II}	3.064 (4)		
O(2)···C(1-4)^{II}	3.281 (16)		

[a] For the purposes of clarity, twofold-related atoms are designated by the prime notation. Atoms related by the mirror plane are as follows: Mn(1) and Mn(2), C(1) and C(4), C(2) and C(3), C(2-2) and C(2-6), C(2-3) and C(2-5). [b] The superscripts refer to the following symmetry transformations: (I) $1 - x, y, 1 - z$; (II) $x, 1/2 - y, z - 1/2$.

Results and Discussion

General Description of the Crystal and Molecular Structure. Crystalline di-μ-diphenylsilyl-bis(tetracarbonylmanganese) consists of discrete molecules with the configuration depicted in Figure 1.[63] The identical arrangement parallel to the *b* axis of the two molecules in the unit cell (required by the *A2/m* space group symmetry) is shown from a [100] unit cell projection given in Figure 2.[63] The packing of the molecules appears to be primarily dictated by van der Waals forces

(61) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFEE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.
(62) D. L. Smith, PLANES, Ph.D. Thesis (Appendix IV), University of Wisconsin (Madison), 1962.
(63) C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustration," ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

Table III. Equations of Least-Squares Planes, Distances of Atoms from These Planes, and Angles between the Normals of These Planes[a,b]

I. Equations of Planes and Distances (Å) of Selected Atoms from These Planes			
a. Plane I Through Mn(1), Mn(2), Si, and Si′			
$0.8369X - 0.5474Z = 0$			
Mn(1)	0	O(2′)	0.36
Mn(2)	0	C(3)	−0.20
Si	0	C(3′)	0.20
Si′	0	O(3)	−0.36
C(2)	−0.20	O(3′)	0.36
C(2′)	0.20	C(1-1)	−1.44
O(2)	−0.36	C(2-1)	1.54
b. Plane II Through Mn(1), Mn(2), C(1), C(1′), C(4), and C(4′)			
$-0.4703X - 0.8825Z = 0$			
Mn(1)	0	C(4′)	0
Mn(2)	0	O(1)	0.00
C(1)	0	O(1′)	0.00
C(1′)	0	O(4)	0.00
C(4)	0	O(4′)	0.00
c. Plane III Through Mn(1), Mn(2), Si, Si′, C(2), C(2′), C(3), and C(3′)			
$0.8743X - 0.4854Z = 0$			
Mn(1)	0.00	C(3)	−0.10
Mn(2)	0.00	C(3′)	0.10
Si	0.14	O(2)	−0.21
Si′	−0.14	O(2′)	0.21
C(2)	−0.10	O(3)	−0.21
C(2′)	0.10	O(3′)	0.21
d. Plane IV Through Phenyl Ring 1			
$-0.2162X + 0.9729Y - 0.0824Z + 0.1821 = 0$			
C(1-1)	−0.04	C(1-5)	−0.01
C(1-2)	0.01	C(1-6)	0.04
C(1-3)	0.03	Si	−0.18
C(1-4)	−0.02		
e. Plane V Through Phenyl Ring 2			
$0.0633X - 0.9980Z + 1.4858 = 0$			
C(2-1)	−0.01	C(2-5)	0.00
C(2-2)	0.00	C(2-6)	0.00
C(2-3)	0.00	Si	−0.06
C(2-4)	0.00		

II. Dihedral Angles (deg) between Normals to Planes

I	II	84.9
I	III	4.1
II	III	89.0
IV	V	86.1

[a] The equations of the planes are given in an orthogonal ångström coordinate system (X, Y, Z) which is related to the monoclinic fractional unit cell coordinate system (x, y, z) by the transformation $X = ax + cz \cos \beta$, $Y = by$, and $Z = cz \sin \beta$. [b] Unit weights were used for all atoms in the application of the Smith least-squares planes program.[62]

as evidenced by the intermolecular contacts (Table II) which do not indicate any abnormal intermolecular interactions. The only intermolecular nonhydrogen contact less than 3.2 Å is 3.064 (4) Å between O(1) and O(2).

The dimeric molecule may be considered to arise from the junction of two octahedra at a common edge. The six octahedral sites about each manganese are occupied by four carbonyl ligands and by the two bridging silicon atoms such that the two manganese and two silicon atoms form a Mn_2Si_2 rhombus. The crystallographic site symmetry of C_{2h}-$2/m$ for each molecule (with the crystallographic twofold axis coincident with the Mn–Mn vector direction) demands exact planarity of the Mn_2Si_2 rhombus with four identical sides. The $Mn_2(CO)_8Si_2$ fragment approximately conforms to

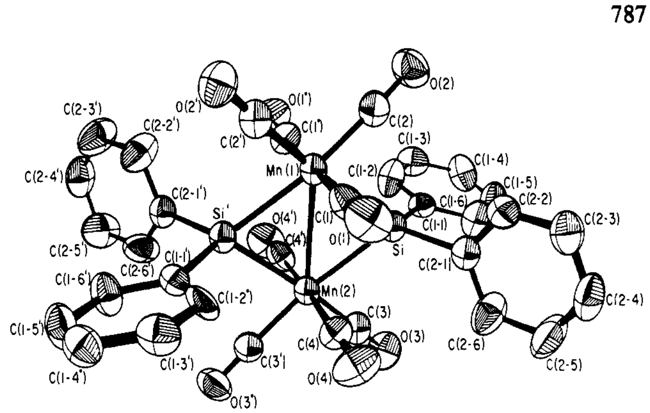

Figure 1. Molecular configuration of $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ which possesses crystallographic site symmetry C_{2h}-$2/m$ such that one phenyl ring attached to each silicon atom is randomly disordered between two crystal orientations. The $Mn_2(CO)_8Si_2$ fragment approximately conforms to D_{2h}-$2/m2/m2/m$ symmetry.

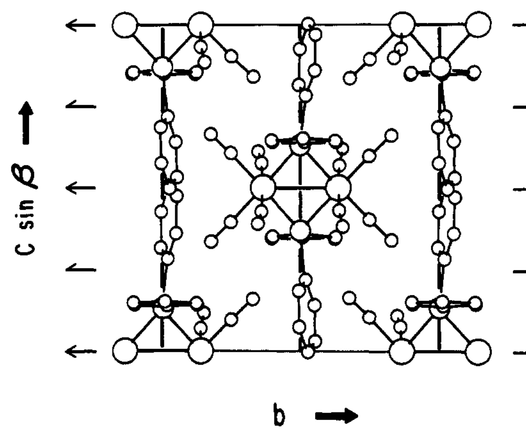

Figure 2. [100] projection of the monoclinic unit cell of symmetry $A2/m$ showing the identical orientations of the two $Mn_2(CO)_8$-$(\mu\text{-}Si(C_6H_5)_2)_2$ molecules.

a D_{2h} geometry. One vertical mirror plane may be defined by the Mn_2Si_2 heterocyclic ring and the four equatorial (in-plane) carbonyl carbon atoms; the maximum perpendicular deviations of these atoms from their mean plane (Table III, c) are 0.14 Å. A second exact vertical mirror plane is defined by the two manganese atoms and four axial (out-of-plane) carbonyl carbon atoms (Table III, b). The dihedral angle between the normals of these two planes is 89.0°, very close to the ideal value of 90° (based on no distortions of the $Mn_2(CO)_8Si_2$ framework from D_{2h} symmetry). Inclusion of the phenyl rings lowers the idealized geometry to C_{2h}-$2/m$. Although the actual molecular symmetry is C_2-2, the crystallographic site symmetry of C_{2h} is achieved by a statistical crystalline disorder of one of the phenyl rings (*vide supra*). The observed angular deformations of the $Mn_2(CO)_8Si_2$ fragment from D_{2h} geometry may be ascribed mainly to intramolecular steric repulsions due to the asymmetrical orientation (relative to the $Mn_2(CO)_8Si_2$ fragment) of the two independent phenyl rings (attached to one silicon atom), which are approximately perpendicular to each other (Figures 1 and 2) as indicated by the dihedral angle between the two normals being 86.1°.

The Mn–Mn Interaction and Its Stereochemical Consequences. The formation of an electron pair Mn–Mn spin-coupling interaction in $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ is required in order that each manganese achieve a closed-shell electronic configuration in harmony with its observed diamagnetism as indicated by the strong ^{1}H nmr signal obtained for the phenyl rings in solution.[43] The formation of a direct electron pair σ bond between the two manganese atoms may occur *via* overlap of the d_{xy} orbitals of each metal atom (*i.e.*, based on a local right-handed Cartesian coordinate system chosen at each Mn atom with the *x* and *y* axes directed approximately toward the two bridging silicon atoms). The distinct metal–metal bond (with probable participation from the appropriate orbitals of the bridging diphenylsilyl ligands) is supported by the observed Mn–Mn distance and the large molecular deformation of the Mn_2Si_2 rhombus.[64–66]

The Mn–Mn distance of 2.871 (2) Å in $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ is similar to the electron pair Mn–Mn distances found in $Mn_2(CO)_{10}$ (2.923 (3) Å)[1] and $Mn_2(CO)_8(P(C_2H_5)_3)_2$ (2.913 (6) Å).[3] These distances are also analogous to the internuclear separation of the manganese atoms observed for the Mn–H–Mn systems in $Mn_2(CO)_8(\mu\text{-}H)(\mu\text{-}P(C_6H_5)_2)$ (2.937 (5) Å)[5] and in $Mn(CO)_4(H_2B_2H_4)Mn_2(CO)_6(\mu\text{-}H)$ (2.845 (3) Å).[67–69] It is important to emphasize, however, that a short metal–metal distance *per se* is not *prima facie* evidence of a direct electron pair metal–metal interaction. In the case of the dimaganetic $[Mn_2(CO)_6(\mu\text{-}N_3)_3]^-$ anion, which was shown by Mason, *et al.*,[70] to conform ideally to a D_{3h} $Fe_2(CO)_9$ type geometry with three azide ligands each bridging two $Mn(CO)_3$ moieties through one nitrogen atom, the short Mn···Mn separation of 2.893 (4) Å is not indicative of a Mn–Mn bond in that a closed-shell electronic configuration already exists for each manganese without the necessity of any electron pair metal–metal interaction. It was suggested[71] that the observed short Mn···Mn distance in this triazide-bridged dimer may be rationalized from steric considerations as a compromise between the nonbonded repulsions of the three small-sized bridging atoms which (in a pincer-like fashion) force the two manganese atoms together and the nonbonded repulsions of the two manganese atoms. These conclusions stress that unusual intramolecular steric effects (which are not considered to be present in $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$) may dominate in certain complexes and thereby may greatly affect the resulting metal–metal distances.

Prime evidence for an electron pair metal–metal interaction in $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ is given by a comparison of the molecular parameters for the Mn_2Si_2 framework with those for the Mn_2Br_2 framework in the structurally analogous $Mn_2(CO)_8(\mu\text{-}Br)_2$[4] which has no electron-pair Mn···Mn interaction. The metal–metal bond in $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ is reflected not only in the bonding Mn–Mn distance but also in the resulting sharply acute Mn–Si–Mn bridging angles of 73.4 (1)° *vs.* the nonbonding Mn···Mn distance of 3.743 (8) Å and the normally occurring obtuse Mn–Br–Mn bond angles of 95.6 (3)° (av) in $Mn_2(CO)_8(\mu\text{-}Br)_2$. Dahl, Rodulfo de Gil, and Feltham[46] have correlated structural data for a variety of ligand-bridged dimers containing four-membered M_2B_2 bridged systems (with and without metal–metal interactions). They noted that an electron-pair metal–metal distance in a M_2B_2 system is governed by the size and effective electronegativity of the metal-bonded bridging ligand atom and pointed out that the influence of a metal–metal electron-pair interaction (as demonstrated from magnetic properties) on the molecular geometry may be detected from the extent of angular deformation of the bridged system as revealed from the much sharper M–B–M bridging angles found for complexes containing metal–metal interactions. Other typical octahedrally coordinated metal dimers possessing planar M_2B_2 ring systems, which are each similarly distorted by a metal–metal interaction to give seven-coordinated metal atoms with resulting acute M–B–M angles and M–M′ distances in the single-bond range, include $Mo_2(CO)_6(P(C_2H_5)_3)_2(\mu\text{-}P(CH_3)_2)_2$ (3.090 (2) Å, 78.2 (1)°)[72] and $Ru_2(CO)_6(Sn(CH_3)_3)_2(\mu\text{-}Sn(CH_3)_2)_2$ (3.116 (3) Å, 71.5 (1)°).[73] In striking contrast, analogous dimers without metal–metal interactions, as evident from a relatively undistorted M_2B_2 geometry with nonbonding metal–metal distances and normal obtuse M–B–M angles, include $Fe_2(CO)_8(\mu\text{-}Ge(C_2H_5)_2)_2$ (3.943 (3) Å, 104.6 (4)°),[74] $Fe_2(CO)_6I_2(\mu\text{-}P(CH_3)_2)_2$ (3.590 (4) Å, 102.6 (2)°),[75] Mo_2Cl_{10} (3.84 (2) Å, 98.6 (5)°),[76] and $Ru_2(CO)_6Br_2(\mu\text{-}Br)_2$ (3.752 (4) Å, 93.7 (2)°).[77] The angular deformation of the Mn_2Si_2 rhombus caused by the Mn–Mn interaction gives rise to a large nonbonding Si···Si separation of 3.852 (3) Å, which is similar to the corresponding B···B distances in other octahedrally coordinated metal dimers containing planar M_2B_2 systems with metal–metal interactions.

Particular angular distortions were also found in the octahedral-like environment about each manganese

(64) A possible alternative spin-pairing model which presumably may account for the observed structural features involves a *strong* superexchange interaction through the bridging ligands. These models are not mutually exclusive, and a well-defined distinction between them does not appear evident on the basis of structural data. From a detailed systematic nmr study of a related series of di-μ-phosphido-dimetallic species of formulas $M_2(CO)_8(\mu\text{-}P(CH_3)_2)_2{}^n$ (where M = Cr, Mo, W; n = 0, −2) and $M_2(CO)_6(\mu\text{-}P(CH_3)_2)_2{}^n$ (where M = Fe, Ru; n = 0, −2), Dessy and coworkers[65] suggested from the measured large increases in $J_{PP'}$ upon reduction to the dianion that the metal–metal bond is maintained in the dianion and that the two electrons are in a low-lying σ-like orbital which encompasses the dimetal–diphosphorus system. A somewhat different unified bonding model depicting the drastic influence of antibonding electrons on the molecular geometries of metal cluster complexes including these dimeric systems has evolved from our structural studies.[66]

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atom. The bond angles subtended at each manganese atom show considerable differences from ideal octahedral coordination only for the silicon and equatorial (in-plane) carbonyl ligands. The Si–Mn–Si′ bond angle of 106.6 (1)° and the diametrically opposite (equatorial)-OC–Mn–CO(equatorial) bond angle of 96.7 (3)° are compensated by an acute Si–Mn–CO(equatorial) bond angle of 78.9 (1)°.

The Manganese–Silicon Bond. Recent investigations of the transition metal–silicon bond by infrared, mass spectral, and X-ray diffraction techniques as well as by molecular orbital calculations have been interpreted in terms of substantial π bonding from the occupied transition metal d_π orbitals to the empty d_π orbitals of silicon.[78–80] The crystallographic evidence is based mainly on a comparison of the observed metal–silicon bond lengths[12–19] with values predicted on the basis of covalent radii. In this connection the structural investigation by Muir[19] of $Zr(h^5\text{-}C_5H_5)_2(Cl)(Si(C_6H_5)_3)$ is particularly appropriate in that an extremely long Zr–Si bond length of 2.813 (2) Å was found in accord with a back-donation π-bonding mechanism not being important for a d^0 Zr(IV) (note well that some π back-bonding would undoubtedly occur, since the actual positive charge on the central metal atom would be less than its formal oxidation state). Furthermore, on comparison of its molecular parameters with those of the d^6 Rh(III) complex $Rh(H)(SiCl_3)(Cl)(P(C_6H_5)_3)_2$ (for which the π-bonding model is operational), Muir[19] noted that the Rh–Si bond length of 2.203 (4) Å is 0.61 Å shorter than the Zr–Si bond length and that this drastic reduction in the metal–silicon distance cannot be ascribed solely to the differing σ-bond radii of Zr(IV) and Rh(III). In order to explain this large bond length difference, Muir[19] considered either that the back-donation π-bonding model was an important factor in stabilizing the Rh–Si bond or that the Rh–Si and Zr–Si σ bonds are very different in nature. He also pointed out that these two effects are not mutually exclusive.

The determined Mn–Si bond length in $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ is 2.402 (2) Å. This value is significantly shorter than the Mn–Si bond length of 2.50 Å found by Hamilton and Corey[17] in $Mn(CO)_5(Si(CH_3)_3)$. This bond length difference suggests that the more electronegative bridging diphenylsilyl ligand in $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ may be a better π acceptor of electronic charge than the terminal trimethylsilyl ligand in $Mn(CO)_5(Si(CH_3)_3)$ in agreement with qualitative orbital energy considerations. It is also noteworthy that the occupied bonding symmetry orbital combination between the manganese atoms (*viz.*, the $(1/\sqrt{2})(3d_{xy} + 3d'_{xy})$ orbital) may also be entangled in bonding with the appropriate in-plane empty d_π orbital of each silicon atom such that metal–metal σ bonding may concomitantly occur partly through the bridging ligands *via* electron delocalization mainly involving a four-centered $d_\pi \rightarrow d_\pi$ metal–silicon interaction.

As a consequence of the metal–metal interaction in $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ producing a severe angular distortion at the silicon atoms (as manifested in the Mn–Si–Mn′ bond angle of 73.4 (1)°), the resulting four-coordination about each silicon atom deviates appreciably from that of a regular tetrahedron. The (phenyl)-C–Si–C(phenyl) bond angle of 104.2 (3)° is somewhat smaller than expected and is evidently the result of considerable repulsions between the phenyl rings and the two $Mn(CO)_4$ moieties. Evidence for an unequal repulsion between two differently disposed phenyl rings relative to the $Mn_2(CO)_8Si_2$ fragment is given by the unsymmetrical variation of the four Mn–Si–C(phenyl) bond angles which range from 117.4 (17) to 125.0 (16)°. The average Si–C(phenyl) distance of 1.892 Å is similar to the Si–C distance determined[19] in $Zr(h^5\text{-}C_5H_5)_2(Cl)(Si(C_6H_5)_3)$ (1.913 (4) Å) and with the sum of the silicon and carbon covalent radii (1.92 Å).

The superior ability of carbonyl ligands to act as π acceptors in organometallic complexes is quite well known. Infrared[81] and structural studies[27] and MO calculations[82] have indicated that a carbonyl group will experience increased π back-bonding from the metal atom when it is located trans to a ligand which is a poorer π acceptor than CO. Thus, the two equatorial carbonyl ligands in $Mn_2(CO)_8(\mu\text{-}SiC_6H_5)_2)_2$ which are trans to the silicon atoms (which is a poorer π acceptor than CO) should be recipients of considerably more d_π–π^* (carbonyl) back-bonding than the axial carbonyls. Examination of the Mn–CO distances clearly reveals this trend with the Mn–CO(equatorial) bond length of 1.805 (5) Å being significantly shorter than the Mn–CO-(axial) bond distance of 1.852 (4) Å in agreement with the premise of increased double bond character in the Mn–CO(equatorial) bond. The two crystallographically independent C–O distances of 1.134 (4) and 1.137 (5) Å are virtually identical in accord with the known insensitivity of carbonyl bond length to bond order when the latter is between two and three.

The mean C–C distance in the two phenyl rings is 1.372 Å, slightly shorter than the well-determined value of 1.398 Å. The intra-ring C–C–C bond angles range from 116.0 (8) to 122.2 (7)°. Both rings are essentially planar with no carbon atom deviating from the mean plane by more than 0.01 Å for the crystal-ordered ring (Table III, d) and by more than 0.04 Å for the crystal-disordered ring (Table III, e).

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