Journal of Organometallic Chemistry, 107 (1976) 323—339
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

POLYSILANE DERIVATIVES OF THE TRANSITION METALS

IV *. THE CRYSTAL AND MOLECULAR STRUCTURES OF TRIMETHYLSILYLPENTACARBONYLRHENIUM, $Me_3SiRe(CO)_5$, AND [TRIS(TRIMETHYLSILYL)SILYL] PENTACARBONYLRHENIUM, $(Me_3Si)_3SiRe(CO)_5$

M.C. COULDWELL, J. SIMPSON **

Department of Chemistry, University of Otago, P.O. Box 56, Dunedin (New Zealand)

and WARD T. ROBINSON

Department of Chemistry, University of Canterbury, Private Bag, Christchurch (New Zealand)

(Received September 29th, 1975)

Summary

The crystal and molecular structures of trimethylsilylpentacarbonylrhenium, $Me_3SiRe(CO)_5$, and [tris(trimethylsilyl)silyl] pentacarbonylrhenium, $(Me_3Si)_3SiRe(CO)_5$ have been determined from three-dimensional X-ray data obtained by counter methods.

$Me_3SiRe(CO)_5$ crystallises in space group $P2_1/c$ of the monoclinic system with four molecules in a unit cell of dimensions: $a = 6.972(4)$, $b = 13.418(6)$, $c = 13.400(5)$ Å, β 91.85(5)°. The observed and calculated densities are 2.11 (±0.01) and 2.12 g cm^{-3} respectively. Block-diagonal least-squares refinement of the structure has led to a final value of the conventional R factor of 0.080 for the 1297 independent reflections having $F_o^2 > 3\sigma(F_o^2)$.

$(Me_3Si)_3SiRe(CO)_5$ crystallises in the triclinic space group $P\bar{1}$ with two molecules in a unit cell of dimensions: $a = 9.131(2)$, $b = 9.358(2)$, $c = 15.931(3)$ Å, α 84.78(2), β 105.46(2), γ 111.99(2)°. The observed and calculated densities are 1.56 (±0.01) and 1.57 g cm^{-3} respectively. Block-diagonal least-squares refinement of the structure has led to a final value of the conventional R factor of 0.060 for the 1149 independent reflections having $F_o^2 > 3\sigma(F_o^2)$.

For both structures, the coordination geometry about the rhenium atom is approximately octahedral, and, about the silicon atom bonded to the rhenium atom, tetrahedral.

---

* For part III, see ref. 1.

** To whom all correspondence should be addressed.

The relative orientations of carbonyl and methyl (or trimethylsilyl) groups, when viewed down the Re—Si bond, appear consistent with minimisation of energy due to non-bonded interactions.

In $Me_3SiRe(CO)_5$ all four of the equatorial carbonyl groups are displaced out of the equatorial plane towards the silicon ligand by about 5°. The Si—Re bond is 2.600(1) Å long.

In $(Me_3Si)_3SiRe(CO)_5$ only one of the equatorial carbonyl groups is displaced out of the equatorial plane towards the silicon ligand by 6°. The Si—Re bond is 2.665(9) Å long.

Introduction

Polysilane derivatives of the transition metals are now well characterised [1-6], and we have recently reported a structural determination of one such compound $(Me_3Si)_3SiMn(CO)_5$ [7]. In this latter study it was shown that the bulky tris(trimethylsilyl)silyl group, $(Me_3Si)_3Si$, has a marked effect on both silicon—metal (Si—M) bond length and coordination geometry in the complex. The Si—Mn bond length in $(Me_3Si)_3SiMn(CO)_5$ was found to correspond to a single bond value. This is in contrast to a variety of other Si—M lengths, which were found to be significantly shorter than the sum of the covalent radii of the contributing atoms, a phenomenon generally, though not universally, attributed to a $(d—d)\pi$ interaction in the Si—M bond [8-12]. Furthermore, displacement of the equatorial carbonyl groups towards the apical, non-carbonyl substituent, which is found to be widespread in trigonal bipyramidal and octahedral carbonyl complexes [12,13], is limited in the case of $(Me_3Si)_3SiMn(CO)_5$ to the two equatorial carbonyls which adopt a staggered conformation with respect to the β-Me_3Si groups of the polysilyl ligand [7].

We have determined the crystal and molecular structures of the rhenium compounds trimethylsilylpentacarbonylrhenium, $Me_3SiRe(CO)_5$ and [tris(trimethylsilyl)silyl]pentacarbonylrhenium, $(Me_3Si)_3SiRe(CO)_5$, which allow a direct comparison of compounds with a monosilyl and polysilyl substituent on the rhenium atom. Few structures have been reported for compounds of the Group IV elements bound to the heavier transition metals [14] and rhenium is no exception [15,16]. One Si—Re bond length has been reported previously [17] but this was in a molecule in which a diphenylsilicon ligand bridged two rhenium atoms, with the added complication of possible hydrogen bridging in the Si—Re bond. The compounds examined here provide the first information as to the length of terminal, covalent Si—Re bonds.

Additional questions are posed as to the stereochemical consequences of the progression from manganese to rhenium. The structures of the parent carbonyls, $M_2(CO)_{10}$ (M = Mn, Re), have been determined in both the solid and gaseous phases. In the solid both structures are identical; the two sets of four equatorial carbonyls adopt a staggered configuration and bend towards the adjacent transition metal atom [18,19]. This conformation persists for gaseous $Mn_2(CO)_{10}$ [20], but an electron diffraction study of $Re_2(CO)_{10}$ [21] reveals an eclipsed structure in which the equatorial carbonyl groups remain bent towards the apical

$Re(CO)_5$ moiety. This observation may best be rationalised in terms of the increased length, albeit marginal, of the Re—Re bond. The findings of this latter study have been disputed [22], but further support for a $D_{4d} \rightarrow D_{4h}$ (staggered → eclipsed) transition is to be found in the results of differential thermal analysis and variable temperature X-ray powder diffraction studies [23], which point to a reversible crystalline phase transition occurring in solid $Re_2(CO)_{10}$ at 365 K. In the structures reported here, it was of particular interest to determine the effect of the increased size of the transition metal atom on the distortions within the molecules in comparison with those observed for the corresponding manganese derivatives [7,24,25].

Experimental

$Me_3SiRe(CO)_5$

The compound was prepared by a hydrogen elimination reaction between Me_3SiH and $Re_2(CO)_{10}$ [26]. It was recrystallised from hexane. Diffraction data were collected from a crystal which was mounted with Araldite inside a glass capillary in a random orientation to minimise decomposition from exposure to X-radiation. Its shape approximated that of a parallelopiped with faces defined by the forms {001}, {010}, and {100}. Crystal dimensions normal to these faces were 0.41, 0.31, and 0.56 mm, respectively.

The crystal was found to be monoclinic on the basis of precession photography using Cu-K_α X-radiation and the space group was uniquely confirmed as $P2_1/c$ from the systematic absences, $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$. Accurate lattice and orientation parameters were obtained from a least-squares refinement of the setting angles of twelve reflections 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. The mosaicity of the crystal 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 [27] ranged from 0.10 to 0.11°. The cell dimensions and other important crystal data for $Me_3SiRe(CO)_5$, which is isomorphous with $Me_3SiMn(CO)_5$ [25], are given in Table 1.

Zirconium filtered Mo-K_α X-radiation, and the $\theta - 2\theta$ scan technique were used to collect the intensities of 1958 independent reflections in the quadrant $hk \pm l$ of reciprocal space for which $0 < 2\theta \leqslant 48°$. A symmetric scan range of 1.60° in 2θ, centred on the calculated peak position [λ(Mo-K_α) = 0.7107 Å] was

TABLE 1

CRYSTAL DATA FOR $Me_3SiRe(CO)_5$

mol. wt. 399.44	Monoclinic
a 6.972(4) Å	Space group $P2_1/c$
b 13.418(6) Å	D_m 2.11(1) g cm^{-3} (by flotation)
c 13.400(5) Å	D_c 2.12 g cm^{-3}
β 91.85(5)°	F (000) 744
V 1252.9 Å^3	μ 103.38 cm^{-1}
$Z = 4$	

composed of 20 steps each of 1 second duration. Stationary crystal, stationary counter background counts of 5 seconds were measured at each end of the scan range. Where necessary, to bring reflections within the linear response range of the scintillation counter, attenuators were automatically inserted in the primary beam. The 5 mm diameter diffracted beam collimator was located with its receiving aperture 23 cm away from the crystal.

During data collection, the intensities of three standard reflections, monitored at regular intervals, dropped uniformly to 91% 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 0.09 and is the factor included to avoid overweighting the more intense reflections. The intensities were then corrected for Lorentz and polarisation effects.

Of the 1958 reflections collected, 1297 had values of F_o^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.

$(Me_3Si)_3SiRe(CO)_5$

The compound was prepared by a salt elimination reaction between $(Me_3Si)_3$-SiLi and $BrRe(CO)_5$ [26]. It was recrystallised from hexane. The crystal used for intensity measurements was a needle of dimensions 0.45 × 0.25 × 0.05 mm and its six faces were identified as $(01\bar{1})$, $0\bar{1}1)$ and the forms $\{001\}$, $\{100\}$.

On the basis of precession photography using Cu-K_α X-radiation the crystal was found to be triclinic, and the space group was confirmed as $P\bar{1}$ by the success of the analysis. Accurate lattice and orientation parameters were obtained from a least-squares refinement of the setting angles of twelve reflections 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. The mosaicity of the crystal 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 0.27 to 0.30°. The cell dimensions and other important crystal data are given in Table 2, together with values for the corresponding manganese complex (vide infra).

Zirconium filtered Mo-K_α radiation, and the $\theta - 2\theta$ scan technique, were used to collect the intensities of 1818 independent reflections in the positive h hemisphere of reciprocal space for which $0 < 2\theta \leqslant 36°$. A symmetric scan range of 1.44° in 2θ, centred on the calculated peak position [λ(Mo-K_α) = 0.7107 Å] was composed of 72 steps each of 1 second duration. Stationary crystal, stationary counter background counts of 18 seconds were measured at each end of the scan range. No reflections required attenuation to bring them within

TABLE 2

CRYSTAL DATA FOR $(Me_3Si)_3SiRe(CO)_5$ AND $(Me_3Si)_3SiMn(CO)_5$

	$(Me_3Si)_3SiRe(CO)_5$	$(Me_3Si)_3SiMn(CO)_5$
mol. wt.	573.91	442.65
Space group	Triclinic $P\bar{1}$	Triclinic $P\bar{1}$
a	9.131(2) Å	9.002(2) Å
b	9.358(2) Å	9.655(2) Å
c	15.931(3) Å	15.639(3) Å
α	84.78(2)°	83.66(1)°
β	105.46(2)°	105.65(1)°
γ	111.99(2)°	114.61(1)°
V	1216.5 Å^3	1189.9 Å^3
Z	2	2
D_m	1.56(1) g cm^{-3} (by flotation)	1.20(3) g cm^{-3} (by flotation and calibrated density gradient tube)
D_c	1.57 g cm^{-3}	1.23 g cm^{-3}
μ	54.85 cm^{-1}	7.94 cm^{-1}
Reduced cell constants		
Matrix	101/010/00 — 1	101/010/00 — 1
a	16.11 Å	15.84 Å
b	9.36 Å	9.68 Å
c	15.94 Å	15.64 Å
α	95.20°	96.35°
β	146.82°	146.73°
γ	97.03°	97.20°

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 36% of their original values. The data were corrected for crystal decomposition in the manner outlined by Ibers [28]. Corrections for background ($p = 0.09$), Lorentz and polarisation effects were carried out as described above for $Me_3SiRe(CO)_5$.

Of the 1818 reflections collected, 1149 had values of F_o^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 the structures *

In the block-diagonal least-squares refinements the function minimised was

---

* Calculations were carried out at the University of Otago using a Burroughs 6712 computer. The data processing program HILGOUT is based on programs DRED (J.F. Blount) and PICKOUT (R.J. Doedens). Numerical absorption corrections were applied using program ABSORB which is a major modification of the program AGNOST (L. Templeton and D. Templeton). Structure factor calculations and least-squares 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. 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.

TABLE 3

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $Me_3SiRe(CO)_5$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	0.2162(1)	0.1886(1)	0.1063(1)	0.0194(3)	0.0045(1)	0.0045(1)	0.0005(1)	−0.0004(1)	−0.0001(1)
Si	0.1974(9)	0.3720(5)	0.1679(5)	0.022(5)	0.0038(4)	0.0051(4)	−0.0005(6)	−0.0006(6)	0.0002(3)
C(1)	0.228(3)	0.051(2)	0.060(2)	0.020(6)	0.007(2)	0.007(2)	0.001(3)	−0.009(3)	0.002(2)
C(2)	−0.037(4)	0.168(2)	0.167(2)	0.023(6)	0.006(2)	0.006(2)	−0.002(3)	0.003(2)	0.002(1)
C(3)	0.082(4)	0.257(3)	0.487(2)	0.017(6)	0.011(3)	0.006(2)	0.001(3)	−0.002(2)	−0.004(2)
C(4)	0.466(4)	0.229(2)	0.052(2)	0.024(6)	0.005(2)	0.006(2)	0.003(3)	−0.000(3)	−0.001(1)
C(5)	0.340(5)	0.158(2)	0.242(2)	0.043(9)	0.005(2)	0.007(2)	−0.003(3)	0.007(3)	−0.001(2)
C(6)	−0.049(4)	0.408(3)	0.208(2)	0.025(7)	0.008(2)	0.011(3)	0.005(3)	0.006(3)	−0.001(2)
C(7)	0.257(5)	0.466(2)	0.069(2)	0.06(1)	0.007(2)	0.006(2)	−0.004(4)	0.002(4)	0.004(2)
C(8)	0.363(4)	0.400(2)	0.277(2)	0.034(8)	0.006(2)	0.007(2)	−0.004(3)	−0.007(3)	0.001(1)
O(1)	−0.252(4)	0.469(2)	0.472(2)	0.08(1)	0.004(1)	0.013(2)	−0.006(3)	−0.009(4)	0.003(1)
O(2)	−0.180(3)	0.157(2)	0.204(2)	0.032(6)	0.009(2)	0.011(2)	−0.001(3)	0.000(3)	0.001(1)
O(3)	0.009(3)	0.221(2)	0.418(1)	0.037(7)	0.015(3)	0.006(1)	−0.005(3)	−0.001(2)	−0.001(1)
O(4)	−0.395(3)	0.262(2)	0.022(2)	0.026(5)	0.013(2)	0.010(2)	0.002(3)	0.004(2)	0.000(2)
O(5)	0.409(3)	0.146(2)	0.318(1)	0.035(6)	0.011(2)	0.007(1)	0.001(3)	−0.004(2)	0.001(1)

[a] The form of the anisotropic ellipsoid is $\exp -[(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

$\Sigma[w(|F_o| - |F_c|)^2]$ 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

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and

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

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

Trimethylsilylpentacarbonylrhenium

The positional parameters of the rhenium atom were obtained from an unsharpened three-dimensional Patterson synthesis. Refinement of these coordinates together with an isotropic temperature factor for this atom gave values of 0.179 and 0.252 for R_1 and R_2 respectively. Two difference Fourier syntheses revealed the coordinates of all the other non-hydrogen atoms. After the application of corrections for crystal absorption and using isotropic temperature factors, refinement of this model converged with R_1 and R_2 equal to 0.088 and 0.109 respectively.

The data were reprocessed with $p = 0.15$. 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 0.080 and 0.098, respectively.

A final difference Fourier synthesis showed no anomalously high peaks. The relative weighting scheme appeared satisfactory since $\Sigma[w||F_o| - |F_c||^2]$ showed only slight dependence on $|F_o|$ and $\lambda^{-1}\sin\theta$. The error in an observation of unit weight is 1.20 electrons. Structure factor calculations for the 661 reflections having $F_o^2 < 3\sigma(F_o^2)$ revealed no anomalies of the type $|F_c| >> |F_o|$. There was no evidence for secondary extinction.

The positional and vibrational parameters obtained from the last cycle of refinement are listed in Table 3. Derived root-mean-square amplitudes of vibration for the atoms are listed in Table 4 and some idea of the orientation of the thermal ellipsoids can be obtained from the diagrams. A list of observed and calculated structure amplitudes for the reflections used in the final refinement can be obtained from the authors.

[Tris(trimethylsilyl)silyl]pentacarbonylrhenium

An unsharpened three-dimensional Patterson synthesis gave the positional parameters of the rhenium atom, and refinement of these coordinates with an isotropic temperature factor gave values for R_1 and R_2 of 0.253 and 0.327 respectively. Successive difference Fourier syntheses together with intermediate cycles of least-squares refinement 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 0.078 and 0.093 respectively.

Because of the reduction in volume of the crystal during data collection, as shown by the deterioration in the three standard reflections (64%), it was not

TABLE 4

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)[a] FOR $Me_3SiRe(CO)_5$

Re	0.198(2)	0.201(2)	0.223(2)
Si	0.185(10)	0.212(8)	0.238(8)
C(1)	0.10(5)	0.26(4)	0.33(3)
C(2)	0.17(3)	0.25(3)	0.27(3)
C(3)	0.17(4)	0.21(3)	0.35(4)
C(4)	0.19(4)	0.24(3)	0.27(3)
C(5)	0.21(4)	0.23(3)	0.35(4)
C(6)	0.18(4)	0.30(4)	0.34(4)
C(7)	0.14(5)	0.30(4)	0.40(4)
C(8)	0.19(4)	0.22(4)	0.34(3)
O(1)	0.17(3)	0.32(3)	0.48(3)
O(2)	0.27(3)	0.29(3)	0.32(3)
O(3)	0.22(3)	0.29(3)	0.39(3)
O(4)	0.23(3)	0.31(3)	0.35(3)
O(5)	0.22(2)	0.31(3)	0.32(3)

[a] The figures provide an indication of the direction of these principal axes of vibration.

possible to make any accurate correction for absorption. Therefore these corrections were not applied at any stage of the refinement. High values for isotropic temperature factors suggested that anisotropic thermal models would be more appropriate for all atoms and block-diagonal least-squares refinement of this model led to final values for R_1 and R_2 of 0.060 and 0.075, 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 $\Sigma[w||F_o| - |F_c||^2]$ showed only slight dependence on $|F_o|$ and $\lambda^{-1}\sin\theta$. The error in an observation of unit weight is 1.34 electrons. Structure factor calculations for the 669 reflections having $F_o^2 < 3\sigma(F_o^2)$ showed no anomalies of the type $|F_c| >> |F_o|$. There was no evidence for secondary extinction.

The positional and vibrational parameters obtained from the last cycle of refinement are listed in Table 5. Derived root-mean-square amplitudes of vibration for the atoms are listed in Table 6 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.

Discussion

Striking similarities between the precession photographs of $(Me_3Si)_3SiRe(CO)_5$ and $(Me_3Si)_3SiMn(CO)_5$, reported in an earlier paper [7], led us to check the reduced cell constants derived for the latter compound. This reduction was found to be in error and correct values for both reduced cells are given in Table 2. Despite their similarity the compounds do not appear isomorphous in that refined atomic parameters for the manganese compound do not provide a satisfactory starting model for refinement of the rhenium derivative. The observed

TABLE 5

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $(Me_3Si)_3SiRe(CO)_5$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	−0.1657(2)	0.0524(1)	0.1633(1)	0.010(1)	0.0109(2)	0.0049(1)	0.0026(2)	0.0014(1)	0.0006(1)
Si(4)	0.134(1)	0.2227(9)	0.2517(5)	0.010(3)	0.012(1)	0.0055(5)	0.003(2)	0.0029(9)	−0.0010(7)
Si(1)	0.285(1)	0.402(1)	0.1623(6)	0.012(3)	0.016(2)	0.0068(6)	−0.002(2)	0.002(1)	0.0017(8)
Si(2)	0.293(1)	0.075(1)	0.3189(6)	0.016(3)	0.015(2)	0.0065(6)	0.006(2)	0.000(1)	−0.0001(8)
Si(3)	0.135(1)	0.366(1)	0.3677(6)	0.021(3)	0.018(2)	0.0060(6)	0.009(2)	0.002(1)	−0.0013(8)
C(1)	−0.380(5)	−0.065(4)	0.103(2)	0.03(2)	0.02(1)	0.004(3)	0.02(1)	−0.002(6)	0.003(4)
C(2)	−0.202(4)	0.013(4)	0.275(2)	0.01(1)	0.026(8)	0.007(3)	0.012(7)	0.004(4)	0.005(3)
C(3)	−0.095(4)	−0.136(4)	0.175(2)	0.006(6)	0.03(1)	0.008(3)	0.010(7)	0.005(3)	0.004(4)
C(4)	−0.107(4)	0.102(3)	0.058(2)	0.020(7)	0.017(5)	0.006(3)	0.007(5)	0.003(4)	0.000(3)
C(5)	−0.232(6)	0.248(3)	0.146(2)	0.059(6)	0.013(9)	0.005(2)	0.005(7)	0.014(3)	−0.002(4)
C(6)	0.307(5)	0.309(4)	0.067(2)	0.02(1)	0.030(7)	0.006(2)	0.007(8)	0.006(4)	−0.001(3)
C(7)	0.169(5)	−0.468(3)	0.111(2)	0.02(1)	0.017(6)	0.013(3)	0.013(7)	0.006(4)	0.012(3)
C(8)	−0.500(5)	−0.477(3)	0.222(2)	0.02(1)	0.015(6)	0.013(3)	−0.005(6)	0.006(5)	−0.001(3)
C(9)	−0.043(4)	0.436(4)	0.342(2)	0.017(9)	0.038(8)	0.009(2)	0.018(7)	0.001(4)	−0.009(3)
C(10)	0.131(5)	0.252(4)	0.470(2)	0.03(1)	0.026(7)	0.005(2)	0.013(8)	0.007(4)	0.002(3)
C(11)	0.330(4)	−0.455(3)	0.395(2)	0.013(9)	0.013(6)	0.013(3)	−0.001(6)	−0.003(4)	−0.010(3)
C(12)	0.353(5)	−0.010(3)	0.233(2)	0.03(1)	0.029(6)	0.010(2)	0.022(7)	0.008(4)	−0.005(3)
C(13)	−0.513(4)	0.195(3)	0.395(2)	0.008(8)	0.018(6)	0.010(2)	0.001(6)	−0.009(4)	−0.004(3)
C(14)	0.181(4)	−0.087(3)	0.389(2)	0.03(1)	0.018(6)	0.007(2)	0.010(7)	0.006(4)	0.002(3)
O(1)	−0.519(3)	−0.136(2)	0.065(1)	0.03(1)	0.023(6)	0.006(2)	0.001(7)	−0.001(4)	0.005(3)
O(2)	−0.232(3)	−0.012(3)	0.342(1)	0.034(8)	0.035(5)	0.007(1)	0.015(5)	0.012(3)	0.003(2)
O(3)	−0.069(3)	−0.239(2)	0.181(1)	0.030(8)	0.020(5)	0.009(2)	0.012(5)	0.001(3)	0.003(2)
O(4)	0.080(3)	−0.129(2)	0.015(1)	0.022(8)	0.021(4)	0.008(2)	0.005(5)	0.003(3)	−0.002(2)
O(5)	−0.242(4)	0.356(3)	0.139(1)	0.032(8)	0.030(6)	0.008(2)	0.010(6)	0.001(3)	−0.002(3)

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

TABLE 6

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)[a] FOR $(Me_3Si)_3SiRe(CO)_5$

Re	0.19(1)	0.213(6)	0.255(3)
Si(4)	0.19(3)	0.21(1)	0.27(1)
Si(1)	0.18(2)	0.27(1)	0.33(2)
Si(2)	0.23(2)	0.24(1)	0.31(2)
Si(3)	0.23(2)	0.27(2)	0.29(2)
C(1)	0.12(7)	0.27(6)	0.43(6)
C(2)	0.17(8)	0.25(4)	0.34(4)
C(3)	0.16(5)	0.28(6)	0.36(5)
C(4)	0.26(7)	0.26(6)	0.26(4)
C(5)	0.12(6)	0.23(6)	0.48(4)
C(6)	0.22(7)	0.30(5)	0.36(5)
C(7)	0.11(8)	0.27(6)	0.45(5)
C(8)	0.15(10)	0.30(6)	0.40(4)
C(9)	0.13(9)	0.27(5)	0.44(4)
C(10)	0.23(5)	0.28(6)	0.33(5)
C(11)	0.10(8)	0.27(7)	0.45(5)
C(12)	0.11(7)	0.38(5)	0.39(5)
C(13)	0.13(9)	0.27(5)	0.43(5)
C(14)	0.24(6)	0.26(6)	0.31(5)
O(1)	0.19(5)	0.27(4)	0.44(4)
O(2)	0.16(6)	0.35(3)	0.38(3)
O(3)	0.16(9)	0.35(4)	0.38(3)
O(4)	0.25(4)	0.29(3)	0.31(4)
O(5)	0.28(4)	0.35(3)	0.36(3)

[a] The figures provide an indication of the direction of these principal axes of vibration.

differences in cell constants must therefore reflect small but significant differences in molecular geometry.

Crystals of both $Me_3SiRe(CO)_5$ and $(Me_3Si)_3SiRe(CO)_5$ consist of discrete molecules, the shortest interatomic distances (not involving H atoms) being 3.20 Å for the monosilyl and 3.11 Å for the polysilyl derivatives, respectively. The atom numbering scheme for $Me_3SiRe(CO)_5$ is defined in Fig. 1 and is used throughout the paper; atoms in the $(Me_3Si)_3SiRe(CO)_5$ molecule are similarly

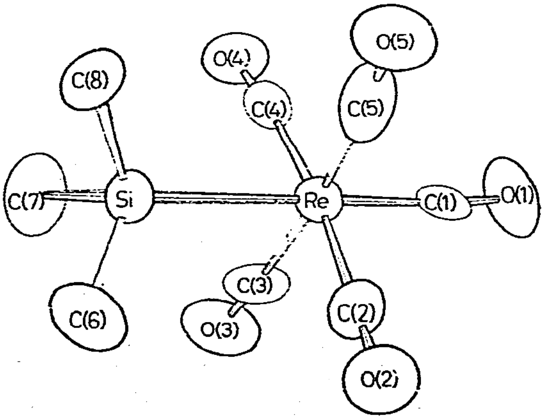

Fig. 1. General view of the $Me_3SiRe(CO)_5$ molecule.

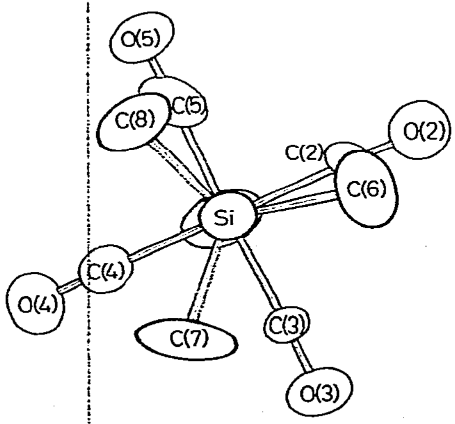

Fig. 2. $Me_3SiRe(CO)_5$ molecule viewed down the Si—Re axis.

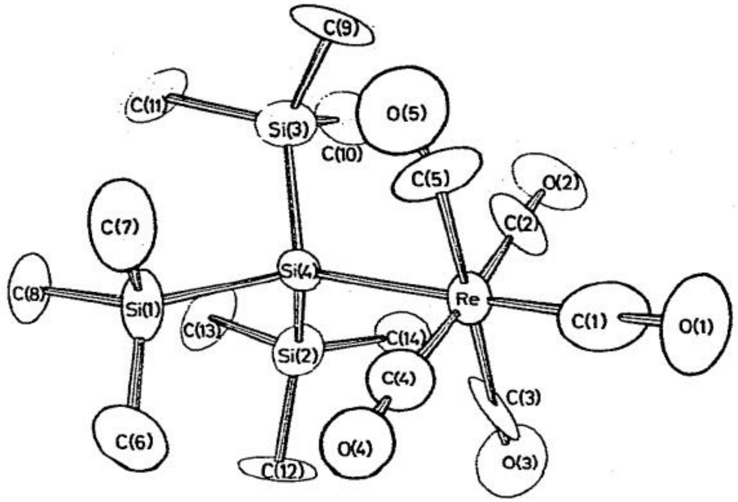

Fig. 3. General view of the $(Me_3Si)_3SiRe(CO)_5$ molecule.

classified in Fig. 3. A second view of both molecules, looking down the Si—Re axes, is given in Fig. 2 for $Me_3SiRe(CO)_5$ and Fig. 4 for $(Me_3Si)_3SiRe(CO)_5$. Selected bonded and non-bonded interatomic distances for $Me_3SiRe(CO)_5$ are given in Table 7 with selected angles of interest in Table 8. For the $(Me_3Si)_3SiRe(CO)_5$ molecule, this information appears in Tables 9 and 10.

The two structures can be conveniently discussed together giving comparisons, where necessary, with the corresponding manganese derivatives [7,24,25]. There are three major areas of interest, the Si—Re bond lengths and the configurations about the rhenium atoms and the apical silicon atoms.

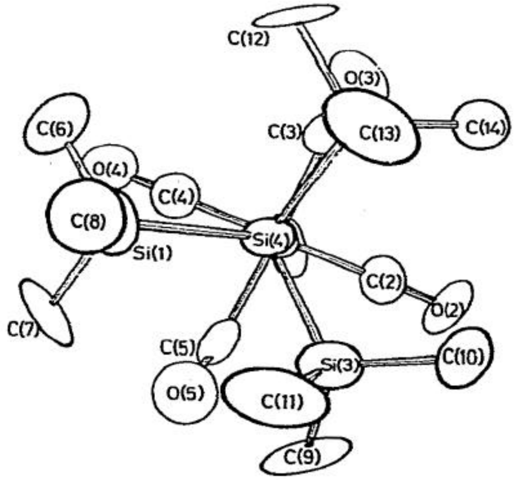

Fig. 4. $(Me_3Si)_3SiRe(CO)_5$ molecule viewed down the Si—Re axis.

TABLE 7

SELECTED BONDED AND NON-BONDED DISTANCES (Å) FOR $Me_3SiRe(CO)_5$

Bonded distances			
Re—Si	2.600(1)	C(1)—O(1)	1.21(3)
Re—C(1)	1.94(3)	C(2)—O(2)	1.13(2)
Re—C(2)	1.99(2)	C(3)—O(3)	1.15(2)
Re—C(3)	1.96(2)	C(4)—O(4)	1.14(3)
Re—C(4)	1.99(3)	C(5)—O(5)	1.12(3)
Re—C(5)	2.02(3)	Si—C(6)	1.88(2)
		Si—C(7)	1.89(3)
		Si—C(8)	1.87(2)
Non-bonded distances (intramolecular)			
Si—C(2)	3.19	C(2)—C(3)	2.77
Si—C(3)	3.06	C(2)—C(5)	2.79
Si—C(4)	3.13	C(3)—C(4)	2.79
Si—C(5)	3.18	C(4)—C(5)	2.88
C(1)—C(2)	2.85	C(2)—C(6)	3.26
C(1)—C(3)	2.92	C(3)—C(7)	3.40
C(1)—C(4)	2.92	C(4)—C(7)	3.50
C(1)—C(5)	2.90	C(5)—C(8)	3.28
Shortest intermolecular non-bonded distance			
O(3)—O(4)	3.20		

The Si—Re bonds

The Si—Re bond lengths observed for the two molecules are shown in Table 11 together with the Si—Mn distances in the corresponding Mn compounds. These results show that the Si—Re bond in $(Me_3Si)_3SiRe(CO)_5$ is significantly longer

TABLE 8

SELECTED ANGLES (DEGREES) FOR $Me_3SiRe(CO)_5$

Bonded angles			
Re—C(1)—O(1)	174(2)	C(6)—Si—C(7)	105(2)
Re—C(2)—O(2)	179(2)	C(6)—Si—C(8)	106(1)
Re—C(3)—O(3)	176(3)	C(7)—Si—C(8)	106(1)
Re—C(4)—O(4)	173(2)		
Re—C(5)—O(5)	177(2)	C(1)—Re—C(2)	93(1)
		C(1)—Re—C(3)	97(1)
Re—Si—C(6)	113(1)	C(1)—Re—C(4)	96(1)
Re—Si—C(7)	113(1)	C(1)—Re—C(5)	94(1)
Re—Si—C(8)	113.7(9)	C(2)—Re—C(3)	89(1)
		C(2)—Re—C(4)	172(1)
Si—Re—C(1)	179.5(7)	C(2)—Re—C(5)	88(1)
Si—Re—C(2)	86.8(8)	C(3)—Re—C(4)	90(1)
Si—Re—C(3)	83(1)	C(3)—Re—C(5)	169(1)
Si—Re—C(4)	84.7(8)	C(4)—Re—C(5)	92(1)
Si—Re—C(5)	86.0(8)		
Dihedral angles [a]			
C(6)—Si—Re Si—Re—C(2)	13.8	C(7)—Si—Re Si—Re—C(4)	47.3
C(8)—Si—Re Si—Re—C(5)	18.7	C(7)—Si—Re Si—Re—C(3)	42.7

[a] Angles are between two planes, each defined by three atoms.

TABLE 9

SELECTED BONDED AND NON-BONDED DISTANCES (Å) FOR $(Me_3Si)_3SiRe(CO)_5$

Bonded distances			
Re—Si(4)	2.665(9)	Si(4)—Si(1)	2.37(1)
Re—C(1)	1.88(4)	Si(4)—Si(2)	2.37(1)
Re—C(2)	1.88(3)	Si(4)—Si(3)	2.38(1)
Re—C(3)	2.07(4)	Si(1)—C(6)	1.91(1)
Re—C(4)	1.86(3)	Si(1)—C(7)	1.89(1)
Re—C(5)	2.11(4)	Si(1)—C(8)	1.90(1)
C(1)—O(1)	1.20(4)	Si(2)—C(12)	1.93(1)
C(2)—O(2)	1.15(3)	Si(2)—C(13)	1.86(1)
C(3)—O(3)	1.08(3)	Si(2)—C(14)	1.93(1)
C(4)—O(4)	1.24(3)	Si(3)—C(9)	1.90(1)
C(5)—O(5)	1.04(3)	Si(3)—C(10)	1.87(1)
		Si(3)—C(11)	1.91(1)
Non-bonded distances (intramolecular)			
Si(4)—C(2)	3.07	C(2)—C(5)	2.92
Si(4)—C(3)	3.36	C(4)—C(5)	2.74
Si(4)—C(4)	3.28	C(2)—C(3)	2.78
Si(4)—C(5)	3.41	C(4)—C(3)	2.78
C(1)—C(2)	2.80	C(2)—C(9)	3.81
C(1)—C(3)	2.84	C(2)—C(12)	3.86
C(1)—C(4)	2.65	C(2)—C(10)	3.88
C(1)—C(5)	2.79	C(2)—C(14)	3.90
C(2)—Si(3)	3.66	C(3)—C(14)	3.62
C(3)—Si(2)	3.60	C(3)—C(12)	3.68
C(4)—Si(1)	3.68	C(4)—C(7)	3.89
C(5)—Si(3)	4.07	C(4)—C(6)	4.04
		C(5)—C(9)	3.42
		C(5)—C(7)	3.78
Shortest intermolecular non-bonded distance			
O(1)—O(1)	3.11		

than that for the monosilyl derivative, an observation that is readily rationalised in terms of the necessity to minimise steric repulsions between the equatorial carbonyl groups and the bulky $(Me_3Si)_3Si$ ligand. The similarity for the Mn and Re systems, between the effects of replacement of the Me_3Si group with the sterically more demanding $(Me_3Si)_3Si$ ligand is striking. In each case, the M—Si bond is extended approximately 0.07 Å in the polysilyl derivatives. Bond distances in molecules of this type are generally investigated by comparing the observed length with that for a covalent single bond. This in turn is estimated by summing the covalent radii for the contributing atoms [7,32]. In the case of rhenium, however, there is a dearth of information on the covalent radius of the formally rhenium(I) atom. In the previous crystallographic determinations of rhenium carbonyl compounds, the covalent radius has been assumed to be given by halving the Re—Re distance in the parent carbonyl, $Re_2(CO)_{10}$ [17,33-35], leading to a rhenium radius of 1.51 Å. This approach has been criticised [32] and certainly, when applied to $Mn_2(CO)_{10}$, predicts a manganese radius some 0.08 Å greater than the currently accepted value [36]. For the compounds $Me_3SiMn(CO)_5$ and $(Me_3Si)_3SiMn(CO)_5$ it was found that while the Si—Mn bond

TABLE 10

SELECTED ANGLES (DEGREES) FOR $(Me_3Si)_3SiRe(CO)_5$

Bonded angles			
Re—C(1)—O(1)	178(3)	Si(4)—Si(1)—C(6)	114(1)
Re—C(2)—O(2)	177(3)	Si(4)—Si(1)—C(7)	109(1)
Re—C(3)—O(3)	175(3)	Si(4)—Si(1)—C(8)	114(1)
Re—C(4)—O(4)	175(3)	Si(4)—Si(2)—C(12)	111(1)
Re—C(5)—O(5)	170(4)	Si(4)—Si(2)—C(13)	111(1)
		Si(4)—Si(2)—C(14)	111(1)
Re—Si(4)—Si(1)	112.6(4)	Si(4)—Si(3)—C(9)	113(1)
Re—Si(4)—Si(2)	113.2(4)	Si(4)—Si(3)—C(10)	112(1)
Re—Si(4)—Si(3)	113.1(5)	Si(4)—Si(3)—C(11)	111(1)
Si(4)—Re—C(1)	178(1)	C(1)—Re—C(2)	96(1)
Si(4)—Re—C(2)	83(1)	C(1)—Re—C(3)	92(1)
Si(4)—Re—C(3)	89(1)	C(1)—Re—C(4)	90(1)
Si(4)—Re—C(4)	91(1)	C(1)—Re—C(5)	88(1)
Si(4)—Re—C(5)	90(1)	C(2)—Re—C(3)	89(1)
		C(2)—Re—C(4)	174(1)
Si(1)—Si(4)—Si(2)	105.9(6)	C(2)—Re—C(5)	94(1)
Si(1)—Si(4)—Si(3)	106.8(5)	C(3)—Re—C(4)	90(1)
Si(2)—Si(4)—Si(3)	104.6(5)	C(3)—Re—C(5)	177(1)
		C(4)—Re—C(5)	87(1)
Dihedral angles [a]			
Si(2)—Si(4)—Re Si(4)—Re—C(3)	12.1	Si(3)—Si(4)—Re Si(4)—Re—C(5)	52.4
Si(1)—Si(4)—Re Si(4)—Re—C(4)	18.3	Si(3)—Si(4)—Re Si(4)—Re—C(2)	41.2

[a] Angles are between two planes, each defined by three atoms.

was appreciably shorter than the calculated single bond value in the Me_3Si derivative [24,25], no significant contraction was observed with the $(Me_3Si)_3Si$ substituent [7]. If this line of argument is extrapolated to the rhenium system, a considerable Si—Re bond shortening would be expected in $Me_3SiRe(CO)_5$ and a maximum value of 1.49 Å may be placed on the covalent radius of the rhenium-(I) atom *. It is interesting to note that the Si—Re distances in both of these molecules are considerably greater than that of 2.54 Å observed in the diphenyl-

TABLE 11

Si—M BOND LENGTHS IN $Me_3SiM(CO)_5$ AND $(Me_3Si)_3SiM(CO)_5$ (M = Mn, Re)

M	$Me_3SiM(CO)_5$ M—Si (Å)	$(Me_3Si)_3SiM(CO)_5$ M—Si (Å)	$\Delta[(Me_3Si)_3Si - Me_3Si]$ (Å)
Mn	2.497(5)[25]	2.564(6)[7]	0.067
Re	2.600(1)	2.665(9)	0.065

---

* Work is currently in progress in these laboratories to test this prediction by determining the structures of rhenium(I) complexes which do not have complicating features such as potential π-acceptor ligands other than CO in the molecule.

silicon bridged rhenium complex $(C_6H_5)_2SiH_2Re_2(CO)_8$ [17]. A similar disparity is observed when terminal [7,24,37] and bridged [22] Mn—Si bonds are compared and has been rationalised in terms of increased π-acceptor properties of the diphenylsilyl ligand and possible electron delocalisation in a multicentred metal—silicon interaction [22].

Configurations about the rhenium atoms

In both these molecules the rhenium atoms are found in distorted octahedral environments (Fig. 1 and Fig. 3). Differences in distortion occur between the two compounds which may best be rationalised in terms of the greater steric requirements of the $(Me_3Si)_3Si$ ligand.

Consideration of the bond angles between the Si—Re and Re—CO (equatorial) vectors shows that for $Me_3SiRe(CO)_5$ the four equatorial carbonyl groups are displaced towards the silicon substituent. The average displacement angle is 5°, marginally less than was found for the corresponding manganese compound. The relative orientations of the methyl groups of the Me_3Si ligand and the equatorial carbonyls are shown in Fig. 2. Consideration of the dihedral angles between planes defined by three atoms shows that the Si—C(7) bond almost exactly bisects the angle subtended at the rhenium atom by the C(3) and C(4) carbonyls. The remaining methyl groups C(6) and C(8) adopt an eclipsed conformation with respect to the C(2) and C(5) carbonyls, but this conjunction does not significantly effect the displacement of these carbonyls out of the equatorial plane.

A similar situation pertains in $(Me_3Si)_3SiRe(CO)_5$ (Fig. 4). One Me_3Si group, Si(3) is staggered with respect to carbonyls C(2) and C(5) while Si(1) and Si(2) adopt partially eclipsed configurations. Deviation from a totally staggered conformation is more marked in this instance, due no doubt to the necessity of minimising non-bonded interactions between the equatorial carbonyl groups and the more bulky Me_3Si substituents. The increased steric requirements of the polysilyl ligand have a marked effect on carbonyl bending in this molecule. Displacement of the equatorial carbonyls towards the apical silicon atom is confined to the C(2) carbonyl, which has a staggered conformation with respect to the β-Me_3Si substituents. Considerable steric interactions exist between the Me_3Si substituents and the remaining carbonyl groups with the result that these are confined, within experimental error, to the equatorial plane.

The errors in Re—CO distances are large, particularly for $(Me_3Si)_3SiRe(CO)_5$ where crystal deterioration during data collection precluded meaningful absorption corrections. The mean Re—CO distances are nonetheless in good agreement for the two molecules; 1.98(3) Å for $Me_3SiRe(CO)_5$ and 1.96(5) Å for $(Me_3Si)_3SiRe(CO)_5$. These compare well with Re—CO bond lengths in other rhenium carbonyls [17,34]. The consistent observation that the Re—CO axial bonds are shorter than the average Re—CO equatorial distances, is of possible significance. Similar observations have been made in a number of other metal carbonyl systems [13,38-40]. The mean C—O distances are unexceptional; 1.15(3) Å for $Me_3SiRe(CO)_5$ and 1.14(4) Å for $(Me_3Si)_3SiRe(CO)_5$ and as expected the Re—C—O angles in both molecules are significantly less than 180°.

Comparison of the M—C distances for the analogous manganese and rhenium compounds is instructive; in $Me_3SiM(CO)_5$, the mean M—C distances are 1.81(1) Å (M = Mn) and 1.98(3) Å (M = Re) while for $(Me_3Si)_3SiM(CO)_5$ mean M—C distances are 1.82(2) Å (M = Mn) and 1.96(5) Å (M = Re). These differences obviously reflect the increase in metal radius from manganese to rhenium but they also have considerable bearing on the causes of carbonyl bending in molecules of this type. The persistance of carbonyl bending towards the apical silicon substituent, despite the presence of bulky polysilyl ligands, is witness to a significant driving force for the displacement process. The effect is generally rationalised in terms of either steric repulsions between the axial and equatorial carbonyl groups or a weak bonding interaction between the carbon atoms of the equatorial carbonyls and the apical, non-carbonyl substituent [12,13]. The fact that this displacement is little affected by passage from manganese to rhenium argues against powerful apical—equatorial carbonyl repulsions as the M—CO apical distance is some 0.1 Å longer for both the mono- and poly-silyl rhenium derivatives. The non-bonded distances between the apical and equatorial carbonyl groups also increase proportionately on progression from manganese to rhenium. It would seem therefore that these observations lend indirect support to the postulate of a bonding interaction between an apical silicon atom and the equatorial carbonyl groups.

Configurations about the silicon atoms

Small but significant deviations from exact tetrahedral environments are found around the apical silicon atoms in both molecules. In $Me_3SiRe(CO)_5$ the mean Re—Si—C bond angle is 113(1)° and the mean C—Si—C angle is 106(2)°. These are close to the values found for $Me_3SiMn(CO)_5$ [25] and $Me_3SiMn(CO)_4PPh_3$ [37]. The average Si—C bonded distance is 1.88(3) Å, which does not deviate significantly from the values found for Me_4Si [41], Me_3SiH [42] or $Me_3SiMn(CO)_4L$ (L = CO [25], PPh_3 [37]).

In $(Me_3Si)_3SiRe(CO)_5$, the mean Re—Si(4)—Si bond angle is 113(1)° and the mean Si—Si(4)—Si bond angle is 106(1)°. The average bonded Si—Si distance is 2.37(1) Å approximately equal to that found in $(Me_3Si)_3SiMn(CO)_5$, but significantly longer than the mean Si—Si bond length of 2.352(3) Å found in $(Me_3Si)_4Si$ [43]. This bond extension in the coordinated polysilane was previously rationalised in terms of steric interactions in the $(Me_3Si)_3SiMn(CO)_5$ molecule [7]. While this explanation may have some validity here, a less marked effect might have been anticipated due to the reduction of steric crowding which must accompany the increased M—Si bond distance in the rhenium system. It is conceivable therefore that the increased length of the Si—Si bonds may be due in part to the involvement of electron density from the apical silicon atoms in weak bonding interactions to the equatorial carbonyl groups at the expense of bonds to the silicon substituents.

Acknowledgement

We wish to thank Dr R.S. Hamilton and Professor E.R. Corey for communicating to us structural data on $Me_3SiMn(CO)_5$ prior to publication. The cooperation of the University of Otago Computing Centre and financial assistance from the Research Committee of the New Zealand Universities Grants Committee are also gratefully acknowledged.

References

1 B.K. Nicholson and J. Simpson, J. Organometal. Chem., 72 (1974) 211.
2 B.K. Nicholson and J. Simpson, J. Organometal. Chem., 32 (1971) C29.
3 R.B. King, K.H. Pannell, C.R. Bennett and M. Ishaq, J. Organometal. Chem., 19 (1967) 327.
4 A. Brookes, S.A.R. Knox and F.G.A. Stone, J. Chem. Soc. A, (1971) 3469.
5 W. Malisch, J. Organometal. Chem., 39 (1972) C28; J. Organometal Chem., 82 (1974) 185.
6 A.G. MacDiarmid, unpublished results quoted in Ref. 3.
7 B.K. Nicholson, W.T. Robinson and J. Simpson, J. Organometal. Chem., 47 (1973) 403.
8 J.F. Young, Advan. Inorg. Chem. Radiochem., 11 (1968) 91.
9 E.H. Brooks and R.J. Cross, Organometal. Chem. Rev., A, 6 (1970) 227.
10 H.G. Ang and P.T. Lau, Organometal. Chem. Rev., A, 8 (1972) 235.
11 C.S. Cundy, B.M. Kingston and M.F. Lappert, Advan. Organometal. Chem., 11 (1973) 253.
12 A.D. Berry, E.R. Corey, A.P. Hagen, A.G. MacDiarmid, F.E. Saalfeld and B.B. Wayland, J. Amer. Chem. Soc., 92 (1970) 1940.
13 R. Bau, S.W. Kirtley, T.N. Sorrell and S. Winarko, J. Amer. Chem. Soc., 96 (1974) 988 and ref. quoted therein.
14 K.W. Muir, J. Chem. Soc. A, (1971) 2663.
15 H.C. Lewis and B.N. Storhoff, J. Organometal. Chem., 43 (1972) 1.
16 Y.T. Struchkov, K.N. Anisimov, O.P. Osipova, N.E. Kolobova and A.N. Nesmayanov, Dokl. Akad. Nauk. SSSR, Ser. Khim., 172 (1967) 107.
17 M. Elder, Inorg. Chem., 9 (1970) 762.
18 L.F. Dahl and R.E. Rundle, Acta Crystallogr., 16 (1963) 419.
19 L.F. Dahl, E. Ishishi and R.E. Rundle, J. Chem. Phys., 26 (1957) 1750.
20 A. Almenningen, G.G. Jacobsen and H.M. Seip, Acta Chem. Scand., 23 (1969) 685.
21 N.I. Gapotchenko, N.V. Alekseev, N.E. Kolobova, K.N. Anisimov, I.A. Ronova and A.A. Johansson, J. Organometal. Chem., 35 (1972) 319.
22 G.L. Simon and L.F. Dahl, J. Amer. Chem. Soc., 95 (1973) 783.
23 P. Lemoine, M. Gross and J. Boissier, J. Chem. Soc. Dalton Trans., (1972) 1626.
24 R.S. Hamilton and E.R. Corey, Abstr. Inorg. Div. 156th Nat. Meeting Amer. Chem. Soc., Atlantic City, N.J., Sept., 1968, No. 025.
25 R.S. Hamilton and E.R. Corey, private communication (1974).
26 J. Simpson, unpublished observations.
27 T.C. Furnas, Single Crystal Orienter Instruction Manual, General Electric Co., Milwaukee, Wis., 1957.
28 J.A. Ibers, Acta Crystallogr., B, 25 (1969) 1667.
29 D.J. Cromer and J.B. Mann, Acta Crystallogr., A, 24 (1968) 321.
30 J.A. Ibers and W.C. Hamilton, Acta Crystallogr., 17 (1964) 781.
31 D.T. Cromer, Acta Crystallogr., 18 (1965) 17.
32 N.C. Baird, Progr. Inorg. Chem., 9 (1968) 1.
33 H.D. Kaesz, R. Bau and M.R. Churchill, J. Amer. Chem. Soc., 89 (1967) 2775.
34 M.R. Churchill and R. Bau, Inorg. Chem., 6 (1967) 2086.
35 M.R. Churchill, P.H. Bird, H.D. Kaesz, R. Bau and B. Fontal, J. Amer. Chem. Soc., 90 (1968) 7135.
36 P.T. Greene and R.F. Bryan, J. Chem. Soc. A, (1971) 1559.
37 M.C. Couldwell and J. Simpson, J. Chem. Soc. Dalton Trans., in press.
38 B.A. Coyle and J.A. Ibers, Inorg. Chem., 11 (1972) 1105.
39 G.L. Simon, A.W. Adamson and L.F. Dahl, J. Amer. Chem. Soc., 94 (1972) 7654.
40 L.D. Brown, K.N. Raymond and S.Z. Goldberg, J. Amer. Chem. Soc., 94 (1972) 7664.
41 W.F. Sheehan and V. Schomaker, J. Amer. Chem. Soc., 74 (1952) 3956.
42 A.C. Bond and L.O. Brockway, J. Amer. Chem. Soc., 76 (1954) 3312.
43 L.S. Bartell, F.B. Clippard and T.L. Boates, Inorg. Chem., 9 (1970) 2436.