SOME DERIVATIVES OF TRIS(DIMETHYLSILYL)METHANE. A NOVEL BICYCLIC TRIS(DISILOXANE) WITH A MANXANE STRUCTURE

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Summary

The compounds $(XMe_2Si)_3CH$ with $X = H$, F, Cl, Br, HO, MeO, EtO and Me_3SiO have been prepared. On heating $(HOSiMe_2)_3CH$ loses water to give $HC(SiMe_2OSiMe_2)_3CH$, 2,2,4,4,6,6,8,8,9,9,11,11-dodecamethyl-3,7,10-trioxa-2,4,6,-8,9,11-hexasila[3.3.3]bicycloundecane. The structure of the latter has been determined by X-ray diffraction and found to be of the manxane type.

Introduction

As part of a programme of study of compounds in which three or four organosilyl groups are attached to a central carbon atom [1], we have prepared species of the type $(XMe_2Si)_3CH$, where $X = H$, F, Cl, Br, OH, OMe, OEt, and $OSiMe_3$. On heating, the compound $(HOMe_2Si)_3CH$ was found to give a novel bicyclic tris(disiloxane), the structure of which has been determined by X-ray diffraction.
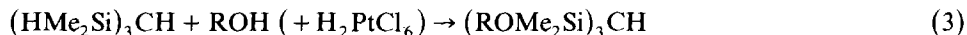
Results and discussion

Reactions

The new compound $(HMe_2Si)_3CH$ was made by treatment of Br_3CH with HMe_2SiCl in the presence of magnesium (eq. 1). Treatment of the purified product with chlorine or bromine in CCl_4 gave the corresponding halides (eq. 2). (These halides were made previously by other methods [2–4], though the bromide was apparently not isolated [4].) The $(HMe_2Si)_3CH$ was also converted into the alkoxy species $(ROMe_2Si)_3CH$ ($R = Me$ or Et) by treatment with the alcohol ROH in the presence of a small amount of H_2PtCl_6 (cf. ref.5) (eq. 3).
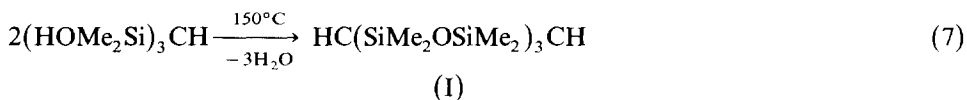
$$HMe_2SiCl + Br_3CH + Mg \rightarrow (HMe_2Si)_3CH \qquad (1)$$

$$(HMe_2Si)_3CH + X_2 \rightarrow (XMe_2Si)_3CH \qquad (2)$$

$$(X = Cl \text{ or } Br)$$

$$(HMe_2Si)_3CH + ROH\ (+H_2PtCl_6) \rightarrow (ROMe_2Si)_3CH \qquad (3)$$

$(R = Me\ or\ Et)$

The bromide $(BrMe_2Si)_3CH$ was treated with $AgBF_4$ in CH_2Cl_2 to give $(FMe_2Si)_3CH$ (eq. 4). It was also hydrolysed in ether to give the corresponding tris-hydroxy product, $(HOMe_2Si)_3CH$ (eq. 5), which was converted into $(Me_3SiOSiMe_2)_3CH$ on treatment with Me_3SiCl (eq. 6). When the tris-hydroxide was heated above its melting point (ca. 98°C) it decomposed with loss of water, and heating of a sample in a sublimation apparatus at 150°C gave the bicyclic tris(disiloxane) 2, 2, 4, 4, 6, 6, 8, 8, 9, 9, 11, 11- dodecamethyl-3,7,10-trioxa-2,4,6,8,9,11-hexasila[3.3.3]bicycloundecane (I) in virtually quantitative yield (eq. 7).

$$(BrMe_2Si)_3CH + AgBF_4 \rightarrow (FMe_2Si)_3CH \qquad (4)$$

$$(BrMe_2Si)_3CH + H_2O \rightarrow (HOMe_2Si)_3CH \qquad (5)$$

$$(HOMe_2Si)_3CH + Me_3SiCl \rightarrow (Me_3SiOSiMe_2)_3CH \qquad (6)$$

$$2(HOMe_2Si)_3CH \xrightarrow[-3H_2O]{150°C} HC(SiMe_2OSiMe_2)_3CH \qquad (7)$$

$$(I)$$

Structure of I

The identity of I was confirmed by a single crystal X-ray diffraction study. The structure is depicted in Fig. 1, which also shows the numbering scheme. The molecule lies on a crystallographic 3-fold axis. It does not have a mirror plane through the O atoms (the torsion angle C(1)–Si(2)---Si(1)–C(2) is 6°), and the point group symmetry is *C*3.

The shape of the bicyclic ring system is similar to that of [3.3.3]bicycloundecane ("manxane") [6,7], all three eight-membered rings having the boat-chair conformation. In the structure shown in Fig. 1 there are two sets of Me groups (respectively on the same and opposite sides of the rings to the nearby oxygen atoms) which are in principle distinguishable, but (unless there is a chance coincidence of chemical shifts) it seems that there is a rapid equilibrium between the degenerate conformers (Ia) and (Ib) *, since even at −90°C only one signal from the Me groups was observed in the

(Ia)   (Ib)

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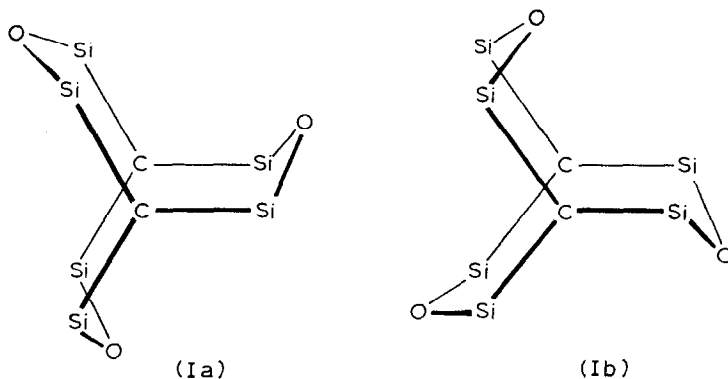
* For clarity hydrogen atoms and methyl groups are omitted in (Ia) and (Ib), and the sharpness of the Si–O–Si angles is exaggerated.
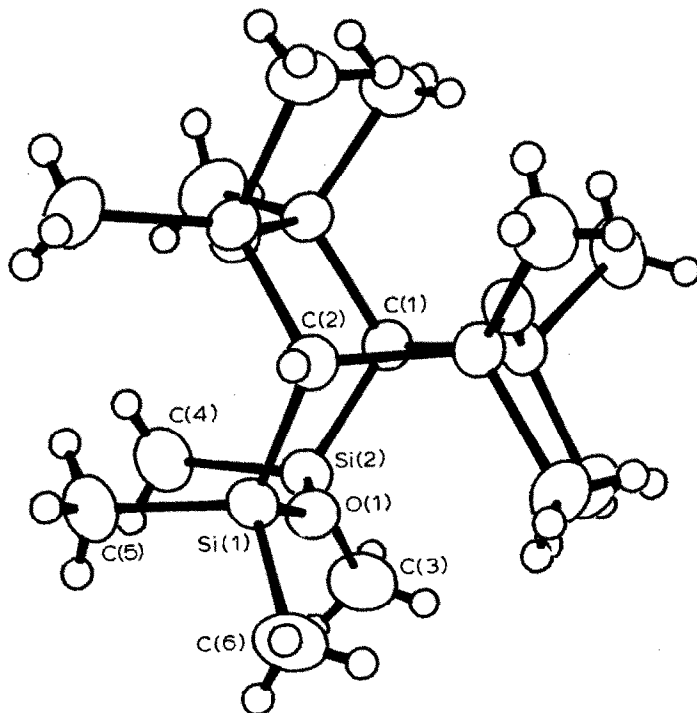
Fig. 1. An ORTEP [17] drawing showing the molecular structure of (I) and atom numbering scheme. Si, C, and O are drawn as 50% thermal vibration ellipsoids and H atoms are drawn as spheres of equal size.

360 MHz ^{1}H NMR spectrum. The interconversion of these conformers would be expected to occur more readily than those of manxane itself (which does give two proton signals at $-80°$C [6]) because of the greater ease of deforming C–Si–O and Si–O–Si than C–C–C angles.

Details of the molecular dimensions are given in Table 1, and some features are as follows: (a) The Si–C–Si angles at the bridgehead C(1) and C(2) carbon atoms have a mean value of 112.8°, close to the values of the corresponding C–C–C angles, viz. 113.5–114.8°, in the hydrochloride of 1-azabicyclo[3.3.3]undecane ("manxine") [8]. These Si–C–Si angles are, however, smaller than those (mean 116.3(4)°) in (Me$_3$Si)$_3$CH [9], and thus probably smaller than those in (HOMe$_2$Si)$_3$CH, so that there is no increase (and there may be a decrease) in the angle strain at the central carbon on dimerization to the bicyclic compound. This is probably an important factor in the ease of forming (I).

(b) The Si–O–Si angle of 145.2(1)° falls within the wide range of such angles observed in cyclic organosiloxanes [10]. The presence of this large angle means that there is much less ring strain than there would be in the corresponding system with CH$_2$ groups in place of the O atoms.

(c) The extracyclic HC–Si–CH$_3$ angles (mean 112.5°) are fairly similar to the C–Si–Me angles in (Me$_3$Si)$_3$CH (II) [9], (Me$_3$Si)$_3$C(SiMe$_2$Ph) (III) [11], and the bicyclic siloxane (IV) [13]. The C(1)–Si(2)–C(3) and C(2)–Si(1)–C(6) angles (mean 111.25°) are significantly smaller than the C(1)–Si(2)–C(4) and C(2)–Si(1)–C(5)

TABLE 1

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Bonds			
Si(1)–O(1)	1.636(1)	Si(1)–C(2)	1.880(5)
Si(1)–C(5)	1.852(2)	Si(1)–C(6)	1.855(2)
Si(2)–O(1)	1.632(1)	Si(2)–C(1)	1.872(5)
Si(2)–C(3)	1.862(2)	Si(2)–C(4)	1.852(2)
(b) Angles			
O(1)–Si(1)–C(2)	108.4(1)	O(1)–Si(1)–C(5)	108.9(1)
O(1)–Si(1)–C(6)	108.2(1)	C(2)–Si(1)–C(5)	114.2(1)
C(2)–Si(1)–C(6)	111.6(1)	C(5)–Si(1)–C(6)	105.3(1)
O(1)–Si(2)–C(1)	107.9(1)	O(1)–Si(2)–C(3)	108.7(1)
O(1)–Si(2)–C(4)	109.9(1)	C(1)–Si(2)–C(3)	110.9(1)
C(1)–Si(2)–C(4)	113.7(1)	C(3)–Si(2)–C(4)	105.8(1)
Si(1)–O(1)–Si(2)	145.2(1)	Si(2)–C(1)–Si(2)[I] [a]	112.5(1)
Si(1)–C(2)–Si(1)[I] [a]	113.0(1)		

[a] Symmetry element I is z, x, y.

angles (mean 113.95°). The Me–Si–Me angles (mean 105.5°) are significantly below the tetrahedral value, as in compounds II, III and IV. The intracyclic (mean 108.2°) and extracyclic O–Si–C angles (mean 108.6°) are close to the tetrahedral value.

$(Me_3Si)_3CH$

(II)

$(Me_3Si)_3C(SiMe_2Ph)$

(III)

(IV)
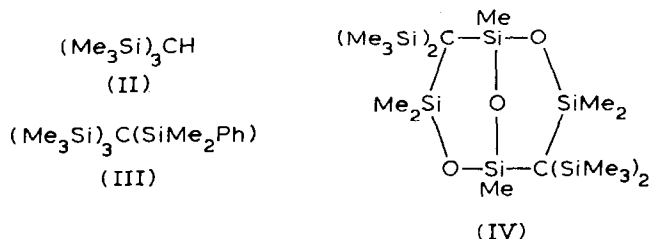
(d) the Me–Si bond lengths (mean 1.855 Å) seem to be significantly shorter than normal, and certainly shorter than the corresponding bonds in II, III and IV, which are in the range 1.87–1.92 Å. The Si(1)–C(2) and Si(2)–C(1) bond lengths (mean 1.876 Å) are rather similar to those (1.877 Å) of the Me_3Si–C bonds in II [9]. The other bond lengths are normal for organosiloxanes [10].

^{13}C NMR Spectra

A feature of interest in the ^{13}C NMR spectra of I and all the $(XMe_2Si)_3CH$ compounds examined in $CDCl_3$ is that the values of $^1J(CH)$ for the methine carbon atom fall in the range 98–103 Hz. The actual values are for I 103, and for $(XMe_2Si)_3CH$: (X =)H, 99; Me, 100; F, 100; Br, 103; MeO, 99; EtO, 98 Hz. The value for $(HOMe_2Si)_3CH$ in $(CD_3)_2CO$ is 96 Hz. It is attractive to relate these low coupling constants to the large Si–C–Si angles in these species, and thus to a high degree of s character in the Si_3C–H bond (cf. ref. 9), but since the corresponding $^1J(CH)$ values for t-Bu_3CH [13] and manxine hydrochloride [8], which have central C–CH–C angles of 116.0° and 113.5–114.8° respectively, are 124 and ca. 121 Hz,

respectively, i.e. "normal" values for sp^3 hydridized carbon, it seems that polarity of the Si–C bonds is predominantly responsible for the observed $^1J(CH)$ values (cf. ref. 14). Interestingly, however, the corresponding $^1J(CH)$ value for $(Me_3Sn)_3CH$ is 123 Hz [15].

Experimental

Spectra

All δ values are in ppm. The ^1H NMR spectra refer to CCl_4 solutions with internal CH_2Cl_2 as lock, except for $(HOMe_2Si)_3CH$ which was examined in $(CD_3)_2CO$ with internal $SiMe_4$ as reference. For the ^{13}C NMR spectra $CDCl_3$ was used as solvent and lock (except for $(HOMe_2Si)_3CH$, which was examined in $(CD_3)_2CO$) and Me_4Si as external reference. The ^{29}Si NMR spectra were recorded with solutions in $CDCl_3$ with Me_4Si or $(Me_3Si)_2O$ as external reference (all values are relative to Me_4Si), and the ^{19}F spectra in CCl_4 (values relative to external $CFCl_3$). Mass spectra were recorded at 70 eV.

(HMe₂Si)₃CH

A solution of $CHBr_3$ (84.2 g, 0.33 mol) in THF (100 cm³) was added under nitrogen to a mixture of HMe_2SiCl (94.5 g, 1.0 mol) and Mg turnings (24.3 g, 1.0 mol) in THF (275 cm³) at such a rate as to maintain gentle reflux. When the addition was complete the mixture was refluxed for 2 h, then cooled and added to ice. The organic layer was separated and washed twice with water (50 cm³), and the aqueous layers were shaken with pentane (2 × 50 cm³). The organic solutions were combined and dried ($MgSO_4$), and the solvent was evaporated. Fractional distillation of the residue gave $(HMe_2Si)_3CH$ (31.4 g, 50%), b.p. 53°C/9 mmHg, 79°C/39 mmHg; $\nu(SiH)$ 2090 cm^{-1}; ^1H NMR: δ −0.78 (q, 1H, CH), 0.15 (d, 18H, Me), 4.05 (m, 3H, SiH); ^{13}C NMR: δ −1.68 ($SiMe_2$, $^1J(CH)$ 120.5 Hz), −2.92 (CH, $^1J(CH)$ 99 Hz); ^{29}Si NMR, δ −15.4 ($^1J(SiH)$ 185 Hz); the mass spectrum showed very large peaks at 175 ($[M - Me]^+$) and 115 ($[M - H - Me_3SiH]^+$), and other prominent peaks at 189 ($[M - H]^+$), 101 ($[M - Me - Me_3SiH]^+$), 73 ($[SiMe_3]^+$) and 59 ($[Me_2HSi]^+$) (Found: C, 43.8; H, 11.4. $C_7H_{22}Si_3$ calcd.: C, 44.1; H, 11.6%).

(MeOMe₂Si)₃CH

Two drops of 0.04 M H_2PtCl_6 in EtOH were added to a solution of $(HMe_2Si)_3CH$ (1 g, 5.3 mmol) in MeOH (25 cm³). The mixture was refluxed for 20 h, during which four more drops of the H_2PtCl_6 solution were added. The solution was filtered, the solvent evaporated off, and the residue distilled to give $(MeOMe_2Si)_3CH$ (0.90 g, 61%), b.p. 76°C/2 mmHg (lit. [5], 130°C/40 mmHg); ^1H NMR: δ −0.06 (s, 1H, CH), 0.16 (s, 18H, $SiMe_2$), 3.34 (s, 9H, OMe); ^{13}C NMR: δ 0.33 ($SiMe_2$, $^1J(CH)$ 118 Hz), 10.4 (CH, $^1J(CH)$ 98.9 Hz), 49.4 (OMe, $^1J(CH)$ 141 Hz).

(EtOMe₂Si)₃CH

This was made from EtOH by the method used for the methoxy analogue, and had b.p. 64°C/0.15 mmHg; NMR; δ −0.08 (s, 1H, CH), 0.19 (s, 18H, $SiMe_2$), 1.16 (t, 9H, CH_2CH_3), 3.58 (q, 6H, OCH_2); ^{13}C NMR: δ 0.94 ($SiMe_2$, $^1J(CH)$ 118 Hz), 10.78 (CH, $^1J(CH)$ 98 Hz), 18.20 (CH_2CH_3, $^1J(CH)$ 125 Hz), 57.46 (OCH_2, $^1J(CH)$ 140 Hz).

(ClMe$_2$Si)$_3$CH

Chlorine was bubbled gently into a stirred solution of (HMe$_2$Si)$_3$CH (1 g) in CCl$_4$ (10 cm^3) until the colour persisted. The solvent was removed to leave the (ClMe$_2$Si)$_3$CH as an oil; ^{1}H NMR: δ (ppm) 0.65(s) (lit. [3], 0.62 (CH) and 0.74 (SiMe$_2$); we could not detect the CH signal).

(BrMe$_2$Si)$_3$CH

A 1 M solution of Br$_2$ in CCl$_4$ was added dropwise to a stirred solution of (HMe$_2$Si)$_3$CH (1 g) in CCl$_4$ (10 cm^3) until the colour persisted. The solvent was evaporated off, and the residue sublimed to give (BrMe$_2$Si)$_3$CH, m.p. 65°C, as the sole product; ^{1}H NMR: δ 0.89 (lit. [4], 0.64 (CH), 0.85 (SiMe$_2$Br) (the product reported in ref. [4] was not isolated; we observed a resonance at δ 0.64 in the crude product but not in the sublimed material); ^{13}C NMR: δ 15.40 (CH, ^1J(CH) 103 Hz), 3.96 (SiMe$_2$, ^1J(CH) 118 Hz).

(FMe$_2$Si)$_3$CH

Silver tetrafluoroborate (4.4 g, 18 mmol) was added to a solution of (BrMe$_2$Si)$_3$CH (2.5 g, 5.8 mmol) in dry CH$_2$Cl$_2$ (100 cm^3) and the mixture was stirred under N$_2$ for 2 h. The salts were filtered off and the solvent was removed under reduced pressure from the filtrate. The residue was distilled to give (FMe$_2$Si)$_3$CH (Found: C, 34.4; H, 7.4. C$_7$H$_{19}$F$_3$Si$_3$ calcd.: C, 34.3; H, 7.8%); ^{1}H NMR (360 MHz): δ 0.33 (d, 18H, Me), 0.39 (q, 1H, CH); ^{13}C-{^{1}H} NMR: δ 1.79 (d, ^2J(CF) 15.5 Hz, SiMe$_2$), 14.3 (d, ^2J(CF) 12 Hz, CH); ^{19}F NMR: δ 149.5(m); mass spectrum (relative intensities in parentheses), m/e 229 ([M − Me]$^+$ 96); 137 (33), 133 (68), 129 (26), 77 ([SiMe$_2$F]$^+$, 100), 73 ([SiMe$_3$]$^+$, 52), 59 (38).

(HOMe$_2$Si)$_3$CH

Aqueous NaOH (10 cm^3 of 0.5 M solution) was added dropwise with stirring during 10 min. to a solution of (BrMe$_2$Si)$_3$CH (1 g) in ether (10 cm^3) kept at 0°C. The stirring at 0°C was continued for 30 min., the layers were separated, and the aqueous layer was extracted with ether (10 cm^3). The ethereal solutions were dried over CaSO$_4$ at 0°C, and the solution was then filtered and evaporated to leave (HOMe$_2$Si)$_3$CH, m.p. 97–98°C, which from its ^{1}H NMR spectrum (in (CD$_3$)$_2$CO) seemed to be pure; δ 0.05 (s, 1H, CH), 0.20 (s, 18H, SiMe$_2$), 2.76 (br.s., 3H, OH); ^{13}C NMR; δ 3.96 (SiMe$_2$, ^1J(CH) 118 Hz), 15.35 (CH, ^1J(CH) 96 Hz).

(Me$_3$SiOMe$_2$Si)$_3$CH

An excess of Me$_3$SiCl was added to a solution of (HOMe$_2$Si)$_3$CH in THF. Removal of the volatile material left a solid, which from its ^{1}H NMR spectrum was apparently (Me$_3$SiOMe$_2$Si)$_3$CH; δ −0.14 (s, 1H, CH), 0.05 (s, 27H, SiMe$_3$), and 0.14 (s, 18H, SiMe$_2$).

HC(SiMe$_2$OSiMe$_2$)$_3$CH (I)

A sample of (HOMe$_2$Si)$_3$CH (1 g) was heated at 150°C in a sublimation apparatus. Droplets of water which formed on the cold finger were pumped away under vacuum, and sublimation was then carried out normally to give I in virtually quantitative yield; m.p. (sealed tube) 275–276°C; ^{1}H NMR: δ −0.85 (s, 2H, CH) and 0.18 (s, 36H, SiMe$_2$); ^{13}C NMR: δ 6.43 (SiMe$_2$, ^1J(CH) 118 Hz), 13.73 (CH, ^1J(CH) 103 Hz) (Found: C, 39.4; H. 8.9. C$_{14}$H$_{38}$O$_3$Si$_6$ calcd.: C, 39.8; H, 9.1%).

Determination of structure of I

Crystal data: $C_{14}H_{38}O_3Si_6$, $M = 423.0$, rhombohedral, a 10.629(5) Å, α 93.48(5)°, U 1193.9 Å^3, $Z = 2$, D_c 1.18 g cm^{-3}, $F(000) = 460$. Mo-K_α radiation, λ 0.71069 Å, μ 3.5 cm^{-1}. Space group $R\bar{3}$ from successful structure refinement.

Data were measured on an Enraf–Nonius CAD4 diffractometer using a crystal of size ca. $0.3 \times 0.3 \times 0.3$ mm obtained by recrystallization from MeOH. Preliminary cell dimensions were found using the SEARCH and INDEX routines of the CAD4 and final values were calculated from the setting angles for 25 reflections with $\theta \approx 15°$. Intensities for $h \pm k \pm l$ reflections with $2 < \theta < 25°$ were measured by a $\theta/2\theta$ scan with a scan width of $\Delta\theta = (0.8 + 0.35\tan\theta)°$. The scan rate for each reflection was determined by a rapid pre-scan at 10° min^{-1} in θ at which point any reflection with $I < \sigma(I)$ was coded as unobserved. The remaining reflections were re-scanned at such a speed as to give a minimum value of $\sigma(I)/I$ of 0.05 subject to a maximum scan time of 60 seconds. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lp effects but not for absorption, and, after averaging any equivalent reflections, 1254 reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement. The values of $\sigma(F^2)$ were taken as $[\sigma^2(I) + (0.02I)^2]^{1/2}/\text{Lp}$.

The structure was initially solved in space group $R3$ by the usual heavy atom methods, but it was then apparent that it was consistent with space group $R\bar{3}$ and all further calculations were done in $R\bar{3}$. Refinement of non-hydrogen atoms with anisotropic temperature factors was by full matrix least squares. Hydrogen atoms

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$ for Si, O, C and $\times 10^3$ for H) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	x	y	z
Si(1)	2619.3(5)	2825.4(5)	4740.3(4)
Si(2)	741.6(5)	1115.5(5)	2912.8(5)
O(1)	1914(1)	1602(1)	3922(1)
C(1)	1286(5)	1286	1286
C(2)	3689(5)	3689	3689
C(3)	286(2)	−567(2)	3161(2)
C(4)	−665(2)	1998(2)	3242(2)
C(5)	1406(2)	3797(2)	5416(2)
C(6)	3518(2)	2252(2)	6119(2)
H(1)	83(5)	83	83
H(2)	417(5)	417	417
H(3A)	−27(2)	−91(2)	248(2)
H(3B)	91(3)	−105(3)	314(3)
H(3C)	−24(3)	−64(2)	374(3)
H(4A)	−83(2)	190(2)	402(2)
H(4B)	−57(2)	284(2)	310(2)
H(4C)	−131(2)	171(2)	277(2)
H(5A)	181(2)	450(2)	596(2)
H(5B)	102(2)	333(2)	588(2)
H(5C)	81(2)	409(2)	473(2)
H(6A)	398(3)	166(3)	602(3)
H(6B)	304(2)	197(3)	660(3)
H(6C)	413(3)	275(3)	647(3)

were located on a difference map and included in the least squares with isotropic temperature factors. The C and H atoms lying on the 3-fold axis had their x coordinate refined with y and z reset to equal x at the end of each cycle of refinement, and temperature factors for these atoms were treated in an analagous way. Refinement converged at $R = 0.030$, $R' = 0.041$, when the maximum shift/error was 0.3 and the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map was everywhere featureless.

The structure solution and refinement was done on a PDP 11/34 computer using the Enraf–Nonius Structure Determination Package. Scattering factors for neutral atoms were taken from ref.16. Final atom coordinates are listed in Table 2 and bond lengths and angles are listed in Table 1. Tables of temperature factors and final structure factors are available from the authors.

References

1 For a review see: C. Eaborn, J. Organomet. Chem., 239 (1982) 93.

2 H. Sakurai, K. Tominaga, T. Watanable, and M. Kumada, Tetrahedron Lett., (1966) 5493.

3 H. Burger, R. Mellies, and K. Wiegel, J. Organomet. Chem., 142 (1977) 55.

4 G. Fritz and U. Finke, Z. Anorg. Allgm. Chem., 430 (1977) 121.

5 R.L. Merker and M.J. Scott, J. Org. Chem., 28 (1963) 2717.

6 M. Doyle, W. Parker, P.A. Gunn, J. Martin, and D.D. MacNicol, Tetrahedron Lett., (1970) 3619.

7 N.J. Leonard, Accts. Chem. Res., 12 (1979) 423.

8 N.J. Leonard, J.C. Coll, A.H.-J. Wang, R.J. Missavage, and I.C. Paul, J. Am. Chem. Soc., 93 (1971) 4628; A.H.-J. Wang, R.J. Missavage, S.R. Byrn, and I.C. Paul, J. Am. Chem. Soc., 94 (1972) 7100.

9 B. Beagley, R.G. Pritchard, C. Eaborn, and S.S. Washburne, J. Chem. Soc., Chem. Commun., (1981) 710; B, Beagley and R.G. Pritchard, J. Mol. Struct., 84 (1982) 129.

10 V.E. Shklover and Yu. T. Struchkov, Russian Chem. Rev., 49 (1980) 272.

11 C. Eaborn, P.B. Hitchcock, and P.D. Lickiss, J. Organomet. Chem., 221 (1981) 13; P.B. Hitchcock, ibid., 228 (1982) C83.

12 C. Eaborn, P.B. Hitchcock, and K.D. Safa, J. Organomet. Chem., 222 (1981) 187.

13 H.B. Burgi and L.S. Bartell, J. Amer. Chem. Soc., 94 (1972) 5236; L.S. Bartell and H.B. Burgi, ibid., p. 5239.

14 K.L. Servis, W.P. Weber, and A.K. Willard, J. Phys. Chem., 74 (1970) 3960.

15 T.N. Mitchell and M. El-Behairy, J. Organomet. Chem., 172 (1979) 293.

16 International Tables for X-Ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974.

17 C.K. Johnson, Report ORNL-3794, 1965, Oak Ridge National Laboratory, Oak Ridge, Tennessee.