THERMOLYSIS OF [TRIS(TRIMETHYLSILYL)METHYL](DIPHENYL)- FLUOROSILANE. ISOMERIZATION OF A SILA-OLEFIN INTERMEDIATE *

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Summary

The compound $(Me_3Si)_3CSiPh_2F$ loses Me_3SiF under reflux or on passage through a tube at $450°C$ to give three products, A, B, and C, in approximately 20/20/60 ratio. Products A and B, which are solids, were shown by X-ray crystallographic analysis to be the diastereoisomeric forms of 1-dimethylsila-2-trimethylsilyl-3-[(methyl)(phenyl)sila]indane. From its mass and ^1H NMR spectra, C (a liquid) was tentatively identified as 1,3-bis(dimethylsila)-2-[(dimethyl)(phenyl)silyl]indane. All three products are isomers of the sila-olefin $(Me_3Si)_2C=SiPh_2$, and it is suggested that the latter is first formed by loss of Me_3SiF from $(MeSi)_3CSiPh_2F$, and the equilibrium $(Me_3Si)_2C=SiPh_2 \rightleftharpoons (Me_3Si)(Ph_2MeSi)C=SiMe_2 \rightleftharpoons (Me_3Si)(PhMe_2Si)C=SiMePh \rightleftharpoons (Me_2PhSi)_2C=SiMe_2$ is then rapidly established; internal cyclizations involving addition of aryl C—H bonds across Si=C bonds then occur to give the observed products. Consistent with this is the observation that a mixture of silicon alkoxides, thought to be $(Me_3Si)_2CHSiPh_2OMe$ and its isomers (which would be formed by addition of methanol across the Si=C bonds of the four sila-olefins) is produced when methanol is passed through the hot tube with the $(Me_3Si)_3CSiPh_2F$.

Full structural details are given for compounds A and B. Some features of interest are: (a) the conformation of the 5-membered ring is different in the two diastereoisomers; (b) the exocyclic Si—C—SiMe3 bond angles, of ca. $120°$, are unusually large; and (c) there is a little distortion of the fused benzene ring, which is attributed to the effect of silicon substituents on the hybridization of carbon atoms to which they are attached.


Introduction

We recently reported the preparation [1] and several unusual reactions [2—4] of tris(trimethylsilyl)methyl-silicon compounds, TsiSiRR'X, where Tsi denotes the "trisyl" group, $(Me_3Si)_3C$ [1]. We describe below attempts to convert some of these compounds by thermolytic elimination of Me_3SiX into sila-olefin species, $(Me_3Si)_2C=CRR'$, which might, when the R groups are large, be prevented by steric hindrance from dimerizing. Products consistent with occurrence of such an elimination were observed in the case of $TsiSiPh_2F$.

Results and discussion

Ready sublimation prevented study of the possible decomposition of $TsiSiCl_3$ and various $TsiSiMe_2X$ compounds [1] by heating under reflux, but $TsiSiPh_2F$ was found to decompose under such conditions with evolution of Me_3SiF. The residue gave a complex ^1H NMR spectrum, suggesting that it was a mixture, and so it was subjected to GLC analysis. This showed the presence of three major components, A, B and C (in order of elution) present in ca. 20/20/60 ratio. Samples of all three were separated by preparative scale GLC, A and B being solids, and C a liquid. When the ^1H NMR spectra of these components were separately recorded, it could be seen that all the resonances from the original crude mixture were accounted for, indicating that no $TsiSiPh_2F$ remained and that no other product had been formed in any significant quantity.

None of the ^1H NMR spectra of A, B and C was consistent with the formulation $(Me_3Si)_2C=SiPh_2$. The mass spectra were all very similar (see below), suggesting that all three products were isomeric with $(Me_3Si)_2C=SiPh_2$, and had closely related structures. The elemental analyses for all three products agreed with this composition. The solids A and B were then subjected to X-ray crystallographic analysis (see below), and found to be the diastereoisomers with the structure shown below. The ^1H NMR spectra were then seen to be wholly consistent with these formulae (see Experimental section).


(A) (B) (X (= C?))
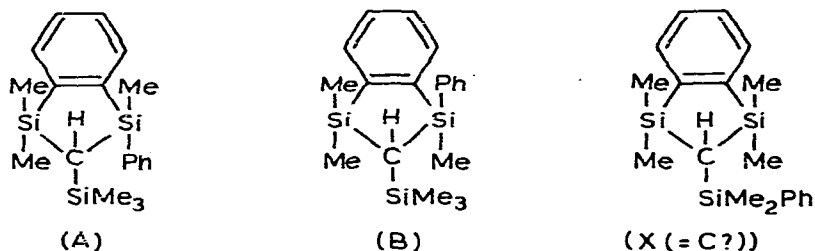
Since C is isomeric with A and B the obvious candidate for its structure is that shown as X above, and this is consistent with the ^1H NMR spectrum (see Experimental section) *. It seems very likely that product C has the structure X, and this will be assumed to be the case in the discussion below.

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* A feature of interest in this NMR spectrum is that two singlets are observed from the $SiMe_2$ groups, presumably because two Me groups are *cis* and two *trans* to the $SiMe_2Ph$ group. Two resonances were also observed for the $SiMe_2$ group of A, but in B this group gave only a singlet.

The thermolysis of TsiSiPh$_2$F was also carried out by passing the vapour in a nitrogen stream through a tube maintained at $450 \pm 10°$C. Analysis by GLC showed that the same three components, A, B and C, were produced in effectively the same ratio as before. The pyrolysis was repeated but with collection of the products in cold methanol, in the hope that some sila-olefin (Me$_3$Si)$_2$-C=SiPh$_2$ might be trapped to give (Me$_3$Si)$_2$CHSiPh$_2$(OMe), but the products were identical with those obtained previously. In a further experiment, methanol was passed through the heated tube along with the TsiSiPh$_2$F, and this gave a quite different product mixture. Its ^{1}H NMR spectrum included 6 singlets in the Si—Me region, and 4 singlets in the SiOMe region, one of them markedly smaller than the other three. The integration ratios for aryl/OMe and aryl/SiMe protons were in acceptable agreement with those expected for a mixture of (Me$_3$Si)$_2$CHSiPh$_2$OMe and its isomers (see below).

It seems very likely that the first step in the pyrolysis is the loss of Me$_3$SiF to give the sila-olefin (Me$_3$Si)$_2$C=SiPh$_2$ *. The simplest route which we can suggest to the products A and B is conversion of this initial sila-olefin into an isomeric sila-olefin by 1,3-migration of a methyl group, followed by addition across the Si=C bond of the C—H bond from an ortho-position of a phenyl group, as in Scheme 1.

SCHEME 1
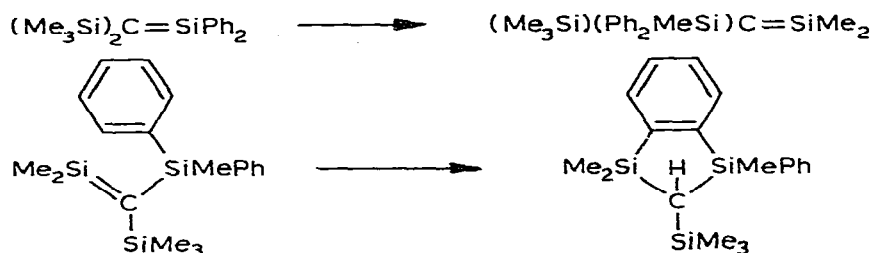
Both of the processes in Scheme 1 are, we believe, without precedent, but they look plausible if the Si=C bond is written in the dipolar from which is believed to contribute largely to its structure [5]. The 1,3-Me migration then bears some analogy to that we have shown to occur in reactions which might be expected to generate siliconium ion centres [3], while the addition of the aryl C—H bond across the Si=C bond could be regarded as a wholly intramolecular electrophilic aromatic substitution (Scheme 2).
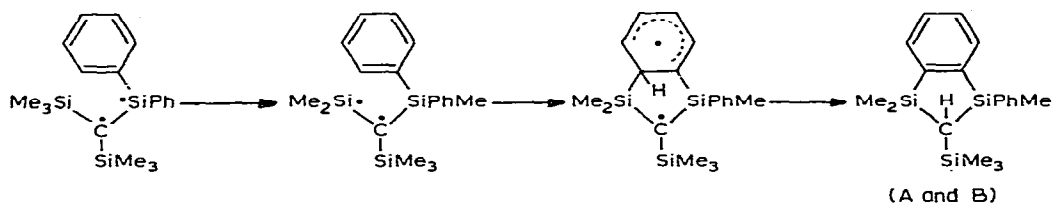
SCHEME 2

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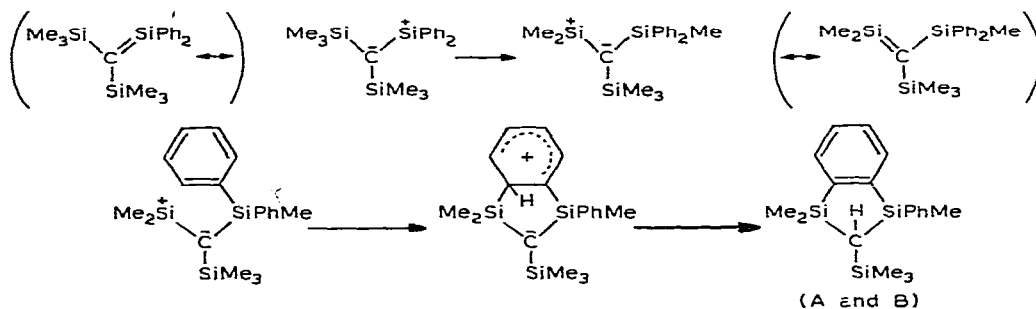
* The reaction can be regarded as related to the sila-olefin forming reactions observed by Wiberg and Preiner [6].

Corresponding processes involving diradical structures can also be written, as in Scheme 3.

SCHEME 3

(A and B)

But, the addition of the C—H across the Si=C bond could also be a synchronous process, avoiding the Wheland carbonium ion or free radical intermediate.

It will be apparent that if, as we postulate, rearrangement of $(Me_3Si)_2C=SiPh_2$ to $(Me_3Si)(Ph_2Me)C=SiMe_2$ by methyl migration occurs readily, then analogous migration of a phenyl group in the latter sila-olefin could be expected to give $(Me_3Si)(PhMe_2Si)C=SiPhMe$, and the migration of a methyl group in the latter to give $(PhMe_2Si)_2C=SiMe_2$. The usual cyclization of the third sila-olefin mentioned would give A and B, as does that of the second, while cyclization of the fourth would give compound X, which we believe to be product C. Thus it seems likely that at the high temperatures used the four possible isomeric olefins are involved in the rapid interconversion process represented in Scheme 4.

SCHEME 4
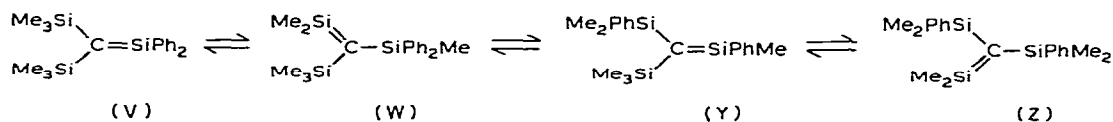
If there were rapid equilibration among the four sila-olefins V, W, Y and Z, then statistical distribution of the 2 Ph and 6 Me groups would give an equilibrium composition of 1 part V, 6 parts W, 12 parts Y, and 9 parts Z. Equal amounts of A and B would be expected from either W or Y (assuming that the latter is a 1 : 1 mixture of the geometrical isomers), while C can be produced only from Z, and V cannot cyclize. If W, Y, and Z cyclized at equal rates, a product ratio of A/B/C of 1/1/1 would be expected. The observed 1/1/3 ratio could be accounted for by assuming that little A or B is, in fact, formed from Y because of greater steric hindrance to addition across a C=SiMePh than across a C=SiMe_2 bond.

The observation of 4 OMe resonances in the ^1H NMR spectrum of the mixture from the pyrolysis in the presence of methanol is consistent with the formation of 4 sila-olefins and subsequent addition of methanol across the double bonds, since the methoxides $(Me_3Si)_2CHSiPh_2OMe$, $(Me_3Si)(Ph_2MeSi)CHSiMe_2$-OMe, $(Me_3Si)(Me_2PhSi)CHSiPhMeOMe$, and $(Me_2PhSi)_2CHSiMe_2OMe$ should be formed. It is tempting to attribute the peak which is markedly smaller than the others to $(Me_3Si)_2CHSiPh_2OMe$, since, as we have seen, at equilibrium olefin V would be present in smaller proportion, but the chemical shift for this peak (δ 3.45 ppm) is the furthest from that previously recorded for the MeO peak of

$(Me_3Si)_2CHSiPh_2OMe$ (viz., δ 3.33 ppm) [2]. It is quite possible, of course, that there is some trapping of the sila-olefins before complete equilibration; certainly, in methanolic sodium methoxide the sila-olefin $(Me_3Si)_2C=SiPh_2$ gives the single addition product $(Me_3Si)_2CHSiPh_2OMe$ [2]. The mixture of 4 silicon methoxides which we postulate could, in principle, give 9 distinct Si—Me resonances, whereas only 6 were resolved, but overlapping is very likely; indeed, one could perhaps only be confident of seeing 5 SiMe signals, one from each of the groupings Me_3Si, $MePh_2Si$, $PhMe_2Si$, $MeOMe_2Si$ and $MeOMePhSi$, possibly with one or more extra signals arising from splitting associated with the pressure of chiral centres in some of the products.

Our interpretations could also be taken to imply that even the sila-olefins $(Me_3Si)(Ph_2MeSi)C=SiMe_2$ and $(PhMe_2Si)_2C=SiMe_2$ go to stable compounds more readily by internal cyclization than by dimerization, although dimerization would be expected to occur fairly easily in these cases in the light of the behaviour of $(Me_3Si)_2C=SiMe_2$ [6]. There is, however, also the less likely possibility that dimerization does occur but is reversible at the high temperature involved (cf. ref. [7]), so that ultimately any sila-olefins appear as internally cyclized products.

Interestingly, the compounds $TsiSiMe_2(O_2CMe)$, $TsiSiMe_2Cl$, $TsiSiPh_2Cl$, $TsiSiCl_3$ and $TsiSiEt_2F$ underwent no reaction on passage through the tube at 450°C. In itself the greater ease of elimination from the diphenyl compound $TsiSiPh_2F$ than the diethyl analogue $TsiSiEt_2F$ could be nicely attributed to stabilization of the forming Si=C bond by conjugation with the phenyl groups, but the ready rearrangement to $(Me_3Si)(Ph_2MeSi)C=SiMe_2$ which we have postulated implies that the olefin would be little, if any, less stable than $(Me_3Si)_2C=SiPh_2$. Possibly the greater crowding in the diphenyl compound $(Me_3Si)_3CSiPh_2F$ and thus the greater relief of steric strain on elimination, is a major factor. The crowding would be even more marked in the case of the chloride $(Me_3Si)_3CSiPh_2Cl$, and so it must be assumed that fluorides are intrinsically superior to chlorides in these eliminations.

Mass spectra

Mass spectral data for products **A**, **B**, and **C** are given in the Experimental section. The main and significant minor peaks (with intensities) observed for $TsiSiPh_2F$ and some related species are as follows:

$TsiSiPh_2F$ (M = 432): 73 (100); 135 (46); 175 (25); 207 (30); 247 (30); 281 (10); 309 (2); 325 (12); 339 (98); 340 (45); 417 (48).

$TsiSiPh_2Br$ (M = 492, based on ^{79}Br): 73 (100); 135 (80); 175 (46); 247 (40); 309 (23); 340 (35); 355 (42); 397 (58); 399 (50, ^{79}Br); 401 (50, ^{81}Br); 477 (23, ^{79}Br); 479 (23, ^{81}Br).

$TsiSiPh_2H$ (M = 414): 73 (100); 135 (41); 175 (21); 247 (13); 321 (43); 339 (11).

$TsiSiPh_2OMe$ (M = 444): 73 (82); 89 (28); 135 (47); 175 (24); 247 (24); 325 (22); 340 (9); 351 (7); 429 (100).

$TsiSiPhMeF$ (M = 370): 73 (28); 135 (13); 175 (17); 201 (33); 247 (11); 263 (22); 278 (6); 355 (100).

$TsiSiPhMeI$ (M = 478): 73 (37); 135 (38); 175 (48); 201 (43); 247 (28); 263 (19); 278 (4); 335 (71); 350 (8); 351 (100); 463 (7).

TsiSiPhMeH (M = 352): 73 (100); 135 (34); 175 (25); 201 (13); 247 (25); 263 (7); 337 (73).

Products A and B showed very weak molecular ions at m/e 340, but C did not. In all three cases the most intense peak was that from $(M - Me)^+$ at 325. The peak at 309 in each case can be attributed to further loss of MeH, i.e. $(M - MeH - Me)^+$, and the appearance of a diffuse metastable ion at ca. 294 is consistent with this; the 309 and 294 peaks are especially intense in C. Of the 3 remaining peaks present in all three cases, those at m/e 73 and 135 can be attributed respectively to Me_3Si^+ and Me_2PhSi^+, while that at 175 could arise by loss of Me_3SiPh from the parent molecules A, B, and C, the observed ion being $(M - Me_3SiPh - Me)^+$.

The peaks at 73, 135, and 175 are present in greater intensity, in the spectra of the $TsiSiPh_2X$ and $TsiSiPhMeX$ species examined. The 175 peak for the Tsi-SiPhMeX species would correspond with $(M - Me_3SiX - Me_4Si - Me)^+$, the loss of Me_4Si paralleling that of Me_3SiPh from $TsiSiPh_2X$ species. For all the $TsiSiPh_2X$ and $TsiSiPhMeX$ compounds the parent ion was missing, but the $(M - Me)^+$ ion was usually strong; the one exception was provided by TsiSiPhMeI, which gave only a weak $(M - Me)^+$ ion, with peaks at 350 and at 335 (strong) which may be associated with $(M - HI)^+$ and $(M - HI - Me)^+$. The base peak in this case, however, is at m/e 351, corresponding to $(M - I)^+$.

The $TsiSiPh_2X$ species with X = F, Br, OMe, and H all show moderate to strong peaks corresponding to $(M - PhH - Me)^+$ at (339, 399, 351, and 321). It is noteworthy that the $TsiSiPh_2X$ compounds with X = F or Br give moderately strong peaks at m/e 340, corresponding with $(Me_3Si)_2C=SiPh_2$ *; for X = F there is also a peak at 325 corresponding with loss of Me from the sila-olefin and a weak peak at 309 corresponding with further loss of MeH, while for X = Br the 325 peak is missing but the 309 peak enhanced. The compound with X = OMe also gives the peaks at 325 and 340, but neither of these peaks is present for X = H, indicating that loss of Me_3SiH is markedly less favourable than loss of Me_3SiX where X = F, Br, or OMe. A fairly strong peak at 397 given by $TsiSiPh_2Br$ corresponds to $(M - HBr - Me)^+$. Quite strong peaks at 247 for X = F, Br, and OMe could correspond with $(M - Me_3SiX - PhH - Me)^+$, arising from loss of PhH from $(Me_3Si)_2C=SiPh_2$, or loss of Me_3SiX from the $(M - PhH)$ species which gives rise to the $(M - PhH - Me)^+$ ions. This 247 peak also appears for TsiSiPhMeX compounds, where it could be associated with the corresponding loss of MeH from $(Me_3Si)C=SiPhMe$, the ion observed being $(M - Me_3SiX - MeH - Me)^+$. The TsiSiPhMeX compounds with X = F, I and H all show a peak at m/e 263 corresponding with $(M - Me_3SiX - Me)^+$ (i.e. with the 325 peak given by the $TsiSiPh_2X$ species).

The ready loss of Me_3SiX in the mass spectrometer from the $TsiSiPh_2X$ (except for X = H) and TsiSiPhMeX species suggests that all of them might give the corresponding sila-olefin on thermolysis under suitable conditions. We note, however, that the ready loss of benzene from $TsiSiPh_2X$ species observed in the mass spectrometer seems not to occur to any significant extent in the thermo-

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* We previously stated that for $TsiSiPh_2F$ the peak at 340 was the base peak [2]. This is incorrect; there is an intense peak (which is sometimes the base peak) at 339, as discussed above.

lysis of TsiSiPh₂F; any benzene generated would have been collected along with the Me₃SiF, which was essentially pure.

Structural details of Products A and B

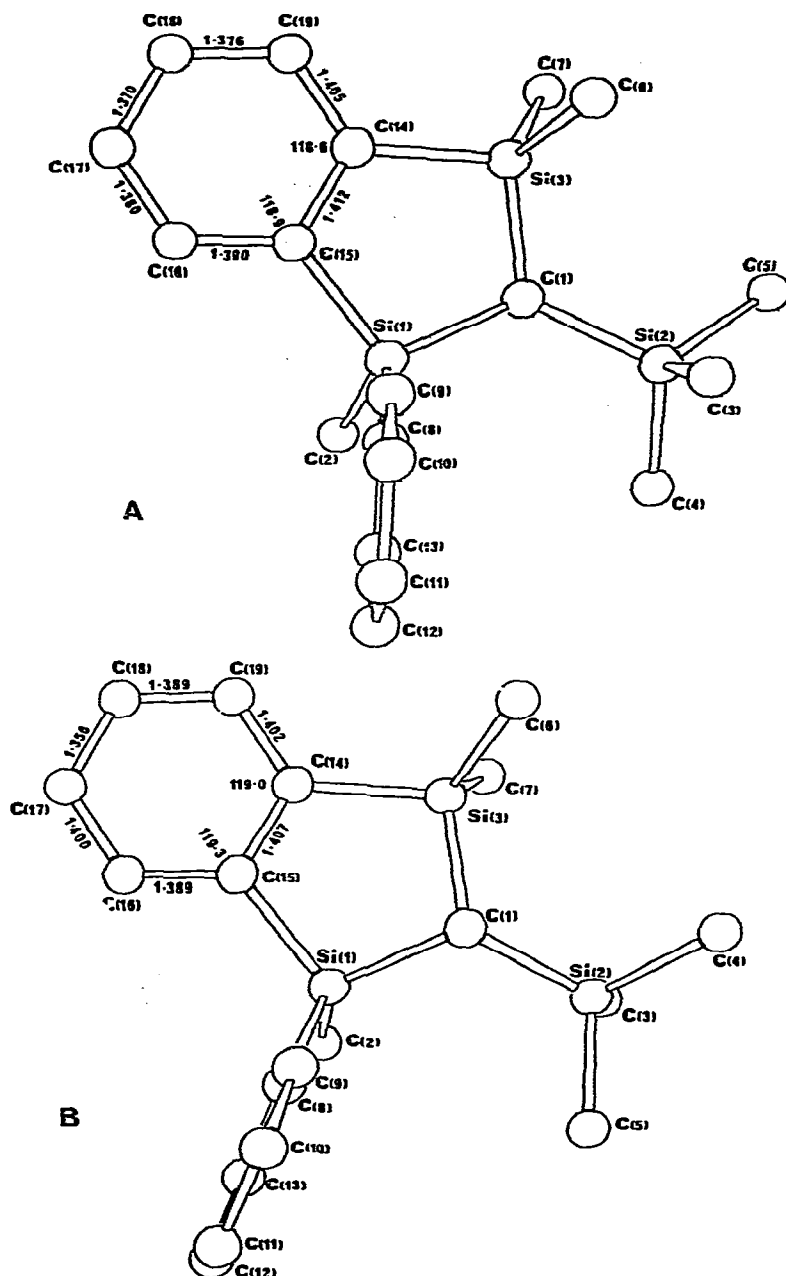The crystal structures clearly show that products A and B are diastereiso-

Fig. 1. Structures of the solid 1,3-disilaindane derivatives produced by thermolysis of (Me₃Si)₃CSiPh₂F.

mers, and that each crystallises in a centrosymmetric space group containing two enantiomers. The molecular conformations and atom numbering schemes are shown in Fig. 1 and the molecular dimensions are listed in Table 2.

The main feature of interest in the structures is that in order to minimize the intramolecular contacts the exocyclic bond angles Si(1)—C(1)—Si(2) and Si(3)—C(1)—Si(2) are exceptionally large, all being close to 120°. A second feature is that the interchange of the SiMe$_3$ and H substituents on C(1) in the two isomers is accompanied by a change of conformation of the five-membered ring, which in each case is an envelope with C(1) the out of plane atom, with the bulky SiMe$_3$ group in the equatorial position, and with a staggered conformation about the C(1)—Si(2) bond. Thus in A, C(1) is below the plane of the five membered ring as viewed in the Fig. 1, whilst in B, C(1) is above the plane. This has the effect on the positions of the Me and Ph substituents of Si(1) and the two Me substituents of Si(3) of a small rotation (mean 18°) about the Si(1)—C(15) and Si(3)—C(14) bonds. There is good agreement between chemically equivalent bond lengths and angles in the two molecules, with average bond lengths of 1.852(10) Å for Si—Me, 1.872(4) Å for Si—Ph, and 1.870(5) Å for the three Si—C(1) bonds. These values are in line with those in similar molecules, e.g. 1.873(7) Å for Si—Ph in tetraphenylsilane [8], and 1.863(5) Å for Si—Me in cyclobis(benzylamidodimethylsilane) [9].

Also noteworthy is the pattern of bond lengths in the C(14)—C(19) benzene ring. The apparent slight shortening of the C(17)—C(18) bond is probably an artifact of molecular vibrations, but the systematic though barely significant lengthening of the C(14)—C(15) bond (mean 1.410(6) Å) and to a lesser extent the C(14)—C(19) bond (mean 1.404(7) Å) seems worthy of comment. This type of effect has been shown to be due to a change in the hybridization at carbon atoms bearing substituents of different electronegativity [10]. The hybrid orbitals of atoms C(14) and C(15) pointing towards the silicon substituents, of lower relative electronegativity, will have more s character, with a concomitant increase in the p character of the orbitals used in bonding to the adjacent ring positions. This will cause a decrease in the endocyclic ring angles at C(14) and C(15) and an increase in the bond length to the adjacent ring carbon atoms. The latter effect will be double for the bond C(14)—C(15), compatible with the observed bond lengths in the ring. The observed endocyclic bond angles at C(14) and C(15), with a mean value of 118.9(2)°, are indeed smaller than the other endocyclic ring bonds. No such changes in geometry are discernable for the other phenyl ring, which has only one silicon substituent. In both molecules the plane of the C(8)—C(13) phenyl ring is nearly at right angles to the plane of the other phenylring (Table 3), perhaps reflecting a preferred conformation based on minimization of intramolecular contacts.

Experimental

General

NMR spectra were recorded at 60 Mhz with solutions in CCl$_4$ containing CH$_2$Cl$_2$ as internal standard.

Mass spectra were recorded at 70 eV.

Starting materials

The preparations of the compounds TsiSiCl₃, TsiSiPh₂F, TsiSiPh₂Cl, TsiSi-Me₂(O₂CCH₃), and TsiSiEt₂F have been described previously [1].

Thermolysis of TsiSiPh₂F under reflux

The TsiSiPh₂F (4.0 g, 0.0090 mol) was placed in a 25 cm³ round bottom flask fitted with thermometer, nitrogen inlet, and reflux air condenser, the top of which was connected to a cold trap. The flask was heated in a metal bath maintained at 340°C and the liquid refluxed gently in a slow stream of nitrogen. A liquid collected in the cold trap, and the temperature of the vapour above the boiling liquid rose gradually during 1 hour to 305°C, and then stayed constant, and heating was discontinued. The liquid collected in the cold trap was identified as Me₃SiF from the IR spectrum of its vapour and by measurement of its molecular weight by weighing of a known volume of the vapour [Found:, 91.5; Calcd., 92]. The ¹H NMR spectrum of the residue in the reaction flask was recorded. GLC analysis indicated that this residue contained three components A, B, and C (in order of increasing retention time) in ratios of ca. 20/20/60, and preparative GLC (20% Antarox C0990 on 80—100 mesh Chromosorb P at 200°C) gave A and B as solids and C as a liquid. All the peaks in the ¹H NMR spectrum of the reaction residue were fully accounted for in terms of the spectra of the separate components (see below), and the integration ratio of aryl to other protons was as expected.

Physical properties and analyses of the components were as follows:

Compound A. M.p. 85°C (Found: C, 66.7; H, 8.0. C₁₉H₂₈Si₃ Calcd.: C, 67.0; H, 8.2%); ¹H NMR spectrum: δ(CCl₄): —0.42 (s, 1H, CH); —0.09 (s, 9H, Me₃-Si); 0.36 (s, 3H) and 0.46 (s, 3H, Me₂Si); 0.75 (s, 3H, MeSi); 7—8 ppm (m, 9H, aryl-H). Mass spectrum (main peaks) *m/e*, (relative intensities in parentheses): 340 (5) [*M*⁺]; 325 (100) [(*M* — Me)⁺]; 309 (13); 295 (4); 175 (7); 135 (9); 73 (9). Exact mass measurements for the high mass peaks gave: 340.14901 (calcd. for C₁₉H₂₈Si₃, 340.14988); 325.12600 (calcd. for C₁₈H₂₅Si₃, 325.12807); 309.09470 (calcd. for C₁₇H₂₁Si₃, 309.09450).

Compound B. M.p. 75°C (Found: C, 66.7; H, 8.0; C₁₉H₂₈Si₃ Calcd.: C, 67.0; H, 8.2%). ¹H NMR spectrum: δ(CCl₄): —0.28 (s, 1H, CH); 0.14 (s, 9H, Me₃Si); 0.42 (s, 6H, Me₂Si); 0.64 (s, 3H, MeSi); 7—8 ppm (m, 9H, aryl-H). Mass spectrum (main peaks) *m/e* (rel. int.): 340 (2) [*M*⁺]; 325 (100) [(*M* — Me)⁺]; 309 (21); 297 (7); 175 (13); 135 (18); 73 (18).

Component C. Liquid. (Found: C, 67.4; H, 8.2. C₁₉H₂₈Si₃ Calcd.; C, 67.0; H, 8.2%). ¹H NMR spectrum: δ: —0.17 (s, 1H, CH); 0.30 (s, 6H, Me₂Si); 0.40 (s, 6H, Me₂Si); 0.56 (s, 6H, Me₂PhSi); 7.2—7.8 ppm (m, 9H, aryl-H). (Of the SiMe₂ signals at 0.30 and 0.40, one is assumed to refer to Me groups *cis* to SiMe₂Ph, and the other to the Me group *trans* to SiMe₂Ph). Mass spectrum (main peaks) *m/e* (rel. int.): 325 (100) (*M* — Me)⁺; 309 (89); ca. 294 (30) (metastable); 175 (62); 135 (96); 73 (78).

Thermolysis of TsiSiPh₂F in hot tube

(a) (Alone) A tube furnace sloping downwards at an angle of 15° from the inlet to the exit end was fitted with a 1.1 m Pyrex glass tube of 2.5 cm internal diameter equipped with a nitrogen inlet and syringe access. The exit of the tube

was connected to a trap cooled in ice-water. The apparatus was brought to
450 ± 10°C at a nitrogen flow of ca. 30 cm³/min. At a nitrogen flow of 5 cm³/
min, a solution of TsiSiPh₂F (50 mg) in light petroleum (b.p. 80—100°C;
5 cm³) was injected dropwise during 5 min, each drop rolling down the tube
and vaporizing instantly upon reaching the heated section. Subsequently addi-
tional light petroleum (3 cm³) was introduced in similar fashion to "rinse" the
tube, and the nitrogen flow was then increased to 15 cm³/min to elute all vola-
tile products. The condensate in the cold trap was rotary evaporated to leave a
semi-solid residue. Analysis of this residue by GLC showed that the three com-
ponents A, B, and C were present in virtually the same proportions as those ob-
served from the liquid thermolysis. Repetition of the experiment with collec-
tion of the products in cold methanol gave the same result.

(b) (In the presence of methanol.) The general procedure described under (a)
was followed, but the TsiSiPh₂F (50 mg) was added during 10 min at a nitrogen
flow of 10 cm³/min as a solution in a mixture of light petroleum (3 cm³), meth-
anol (2 cm³), and acetone (0.5 cm³) (added to give a homogeneous solution).
After a further 5 min the tube was rinsed with light petroleum (5 cm³), and the
nitrogen flow of 10 cm³/min subsequently continued for a further 10 min.

The condensate in the cold trap was taken up in hexane (30 cm³), and the
hexane solution was washed several times with water, then dried and evapo-
rated to leave an oil. The ¹H NMR spectrum of this oil showed multiple peaks
in the aryl-proton region and 4 singlets in the Si—OMe region, at δ 3.38, 3.30,
3.25, and 3.45 ppm (the last smaller than the others) and 6 singlets in the
Si—Me region. The integration ratio for aryl/SiOMe protons was 10/2.9, com-
pared with 10/3 expected for (Me₃Si)₂CHSiPh₂OMe and its isomers and that for
aryl/MeSi protons was 10/17, compared with the 10/18 expected for these iso-
mers. The expected (low intensity) peaks at ca. δ —0.1 ppm for CH protons
were not resolved from background noise.

Attempted thermolysis of TsiSiCl₃, TsiSiMe₂(O₂CMe), TsiSiMe₂Cl, TsiSiPh₂Cl,
and TsiSiEt₂F

A sample of each of these compounds was twice passed through the hot tube
at 450°C under the conditions described under (a) above for TsiSiPh₂F. In each
case the reactant was recovered unchanged, and no products were detected.

X-Ray crystallographic study

Isomer A

Crystal data: C₁₉H₂₈Si₃, MW = 340.7, monoclinic, a 8.173(2), b 28.742(8),
c 8.841(2) Å, β 93.18(2)°, U 2073.6 Å³, Z = 4, Dc 1.09 g cm⁻³, F(000) = 736.
Mo-Kα radiation, μ 2.2 cm⁻¹. Space group P2₁/c from systematic absences of
h0l for l odd and 0k0 for k odd.

The data crystal was a section of size 0.5 × 0.4 × 0.3 mm cut from a needle
crystal, and data were measured on a Hilger and Watts Y290 four circle diffrac-
tometer. Accurate cell dimensions were derived from the setting angles for 12
reflections. Intensities for hk ± l reflections with 2 < θ < 25° were measured
by an ω/2θ step scan using Mo-Kα radiation with a graphite crystal monochro-
mator. Three standard reflections remeasured after every 100 reflections
showed no significant variation. Data were corrected for Lorentz and polarisa-

TABLE 1A

FINAL ATOMIC COORDINATES ($\times 10^4$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES FOR ISOMER A

	x	y	z
Si(1)	2444.6(13)	1184.6(3)	3358.5(11)
Si(2)	8.1(15)	1084.9(4)	344.6(13)
Si(3)	2959.6(14)	1830.0(3)	776.7(12)
C(1)	1400(5)	1446(2)	1626(4)
C(2)	1135(6)	1247(2)	5025(4)
C(3)	1075(6)	623(2)	−658(5)
C(4)	−1576(6)	816(2)	1456(6)
C(5)	−1023(7)	1471(2)	−1102(6)
C(6)	3868(6)	1605(2)	−955(5)
C(7)	2126(7)	2420(2)	393(5)
C(8)	3042(5)	559(2)	3179(4)
C(9)	4317(6)	438(2)	2314(5)
C(10)	4806(5)	−19(2)	2147(6)
C(11)	4030(8)	−361(2)	2861(6)
C(12)	2774(8)	−261(2)	3748(7)
C(13)	2273(7)	203(2)	3907(5)
C(14)	4591(5)	1850(2)	2337(4)
C(15)	4363(5)	1545(2)	3562(4)
C(16)	5523(5)	1540(2)	4771(4)
C(17)	6392(6)	1821(2)	4790(5)
C(18)	7123(6)	2114(2)	3597(5)
C(19)	6000(6)	2131(2)	2380(5)

TABLE 1B

FINAL ATOMIC COORDINATES ($\times 10^4$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES FOR ISOMER B

	x	y	z
Si(1)	1723.1(13)	2284.9(10)	2915.2(6)
Si(2)	4373.3(14)	1789.3(11)	1503.8(7)
Si(3)	2887(14)	4532(11)	1680(10)
C(1)	3534(4)	3079(3)	2198(2)
C(2)	−136(6)	526(5)	2351(3)
C(3)	2719(7)	576(5)	487(4)
C(4)	6434(7)	2923(6)	1065(3)
C(5)	4991(7)	573(5)	2256(4)
C(6)	4859(7)	6237(5)	1671(4)
C(7)	1552(7)	3839(6)	495(3)
C(8)	2724(5)	1983(4)	4045(2)
C(9)	4273(8)	3033(5)	4547(3)
C(10)	5077(9)	2823(7)	5360(4)
C(11)	4345(9)	1576(7)	5710(3)
C(12)	2933(11)	488(8)	5231(5)
C(13)	2002(8)	683(6)	4405(4)
C(14)	1375(5)	4906(4)	2494(2)
C(15)	314(5)	3840(4)	3081(2)
C(16)	−348(5)	3994(5)	3694(3)
C(17)	−923(6)	5217(6)	3745(3)
C(18)	−377(6)	6247(5)	3181(4)
C(19)	759(6)	6107(4)	2549(3)

TABLE 2

INTRAMOLECULAR DISTANCES AND ANGLES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES AND SELECTED TORSION ANGLES

Isomer A		Isomer B	
(a) Bonds (Å)			
Si(1)—C(1)	1.870(4)	Si(1)—C(1)	1.875(3)
Si(1)—C(2)	1.852(3)	Si(1)—C(2)	1.848(5)
Si(1)—C(8)	1.873(6)	Si(1)—C(8)	1.876(3)
Si(1)—C(15)	1.880(5)	Si(1)—C(15)	1.877(4)
Si(2)—C(1)	1.874(5)	Si(2)—C(1)	1.860(3)
Si(2)—C(3)	1.843(5)	Si(2)—C(3)	1.863(6)
Si(2)—C(4)	1.839(5)	Si(2)—C(4)	1.850(6)
Si(2)—C(5)	1.860(6)	Si(2)—C(5)	1.857(5)
Si(3)—C(1)	1.874(5)	Si(3)—C(1)	1.868(3)
Si(3)—C(6)	1.854(5)	Si(3)—C(6)	1.835(5)
Si(3)—C(7)	1.851(6)	Si(3)—C(7)	1.870(5)
Si(3)—C(14)	1.866(4)	Si(3)—C(14)	1.874(4)
C(8)—C(9)	1.371(6)	C(6)—C(9)	1.363(7)
C(8)—C(13)	1.378(7)	C(8)—C(13)	1.379(7)
C(9)—C(10)	1.384(8)	C(9)—C(10)	1.374(8)
C(10)—C(11)	1.345(8)	C(10)—C(11)	1.332(9)
C(11)—C(12)	1.357(9)	C(11)—C(12)	1.348(10)
C(12)—C(13)	1.403(8)	C(12)—C(13)	1.394(10)
C(14)—C(15)	1.412(6)	C(14)—C(15)	1.407(5)
C(14)—C(19)	1.405(7)	C(14)—C(19)	1.402(6)
C(15)—C(16)	1.390(5)	C(15)—C(16)	1.389(6)
C(16)—C(17)	1.380(7)	C(16)—C(17)	1.400(7)
C(17)—C(18)	1.370(7)	C(17)—C(13)	1.356(7)
C(18)—C(19)	1.376(7)	C(18)—C(19)	1.389(7)
(b) Angles (°)			
C(2)—Si(1)—C(1)	111.4(2)	C(2)—Si(1)—C(1)	115.1(2)
C(8)—Si(1)—C(1)	115.2(2)	C(8)—Si(1)—C(1)	111.1(2)
C(15)—Si(1)—C(1)	101.4(2)	C(15)—Si(1)—C(1)	100.8(2)
Si(2)—C(1)—Si(1)	120.4(3)	Si(2)—C(1)—Si(1)	119.3(2)
Si(3)—C(1)—Si(1)	106.0(3)	Si(3)—C(1)—Si(1)	104.6(2)
C(8)—Si(1)—C(2)	108.6(3)	C(8)—Si(1)—C(2)	109.1(2)
C(15)—Si(1)—C(2)	111.6(2)	C(15)—Si(1)—C(2)	109.4(2)
C(15)—Si(1)—C(8)	108.5(2)	C(15)—Si(1)—C(8)	111.3(2)
C(9)—C(8)—Si(1)	120.0(3)	C(9)—C(8)—Si(1)	121.3(3)
C(13)—C(8)—Si(1)	123.0(3)	C(13)—C(8)—Si(1)	123.1(3)
C(14)—C(15)—Si(1)	114.4(3)	C(14)—C(15)—Si(1)	114.1(2)
C(16)—C(15)—Si(1)	126.6(3)	C(16)—C(15)—Si(1)	126.5(3)
C(3)—Si(2)—C(1)	113.7(2)	C(3)—Si(2)—C(1)	114.0(2)
C(4)—Si(2)—C(1)	109.4(2)	C(4)—Si(2)—C(1)	108.8(2)
C(5)—Si(2)—C(1)	108.8(2)	C(5)—Si(2)—C(1)	108.9(2)
Si(3)—C(1)—Si(2)	119.2(3)	Si(3)—C(1)—Si(2)	121.0(2)
C(4)—Si(2)—C(3)	108.7(2)	C(4)—Si(2)—C(3)	107.2(2)
C(5)—Si(2)—C(3)	107.9(2)	C(5)—Si(2)—C(3)	108.9(2)
C(5)—Si(2)—C(4)	108.3(2)	C(5)—Si(2)—C(4)	108.9(2)
C(6)—Si(3)—C(1)	116.0(2)	C(6)—Si(3)—C(1)	112.4(2)
C(7)—Si(3)—C(1)	111.1(2)	C(7)—Si(3)—C(1)	113.9(2)
C(14)—Si(3)—C(1)	101.2(2)	C(14)—Si(3)—C(1)	100.7(2)
C(7)—Si(3)—C(6)	109.1(2)	C(7)—Si(3)—C(6)	109.5(2)
C(14)—Si(3)—C(6)	108.6(2)	C(14)—Si(3)—C(6)	111.3(2)
C(14)—Si(3)—C(7)	110.4(2)	C(14)—Si(3)—C(7)	108.8(2)
C(15)—C(14)—Si(3)	115.4(3)	C(15)—C(14)—Si(3)	114.9(3)
C(19)—C(14)—Si(3)	126.0(3)	C(19)—C(14)—Si(3)	126.1(3)
C(13)—C(8)—C(9)	117.0(6)	C(13)—C(8)—C(9)	115.6(4)
C(10)—C(9)—C(8)	122.2(6)	C(10)—C(9)—C(8)	122.8(5)
C(12)—C(13)—C(8)	121.0(6)	C(12)—C(13)—C(8)	121.0(6)
C(11)—C(10)—C(9)	119.8(5)	C(11)—C(10)—C(9)	121.1(7)

TABLE 2 (continued)

Isomer A		Isomer B	
C(12)—C(11)—C(10)	120.5(6)	C(12)—C(11)—C(10)	118.5(7)
C(13)—C(12)—C(11)	119.6(5)	C(13)—C(12)—C(11)	121.0(7)
C(19)—C(14)—C(15)	118.6(4)	C(19)—C(14)—C(15)	119.0(4)
C(16)—C(15)—C(14)	118.9(4)	C(16)—C(15)—C(14)	119.3(4)
C(18)—C(19)—C(14)	120.8(5)	C(18)—C(19)—C(14)	120.3(5)
C(17)—C(16)—C(15)	121.3(5)	C(17)—C(16)—C(15)	120.4(5)
C(18)—C(17)—C(16)	119.8(5)	C(18)—C(17)—C(16)	120.2(5)
C(19)—C(18)—C(17)	120.5(5)	C(19)—C(18)—C(17)	120.6(5)
(c) Torsion angles (°)			
C(2)—Si(1)—C(1)—Si(2)	−90.3(3)	C(2)—Si(1)—C(1)—Si(2)	−42.3(3)
C(2)—Si(1)—C(1)—Si(3)	130.6(2)	C(2)—Si(1)—C(1)—Si(3)	96.8(2)
C(8)—Si(1)—C(1)—Si(2)	33.9(3)	C(8)—Si(1)—C(1)—Si(2)	82.2(2)
C(8)—Si(1)—C(1)—Si(3)	−105.2(2)	C(8)—Si(1)—C(1)—Si(3)	−138.7(2)
C(15)—Si(1)—C(1)—Si(2)	150.9(3)	C(15)—Si(1)—C(1)—Si(2)	−159.9(2)
C(15)—Si(1)—C(1)—Si(3)	11.8(3)	C(15)—Si(1)—C(1)—Si(3)	−20.8(3)
C(1)—Si(1)—C(8)—C(9)	72.0(4)	C(1)—Si(1)—C(8)—C(9)	43.3(4)
C(1)—Si(1)—C(8)—C(13)	−109.1(4)	C(1)—Si(1)—C(8)—C(13)	−134.1(4)
C(2)—Si(1)—C(8)—C(9)	−162.3(4)	C(2)—Si(1)—C(8)—C(9)	171.1(4)
C(2)—Si(1)—C(8)—C(13)	16.5(5)	C(2)—Si(1)—C(8)—C(13)	−6.3(4)
C(15)—Si(1)—C(8)—C(9)	−40.8(4)	C(15)—Si(1)—C(8)—C(9)	−68.1(4)
C(15)—Si(1)—C(8)—C(13)	138.0(4)	C(15)—Si(1)—C(8)—C(13)	114.5(4)
C(1)—Si(1)—C(15)—C(14)	−7.6(4)	C(1)—Si(1)—C(15)—C(14)	13.6(3)
C(1)—Si(1)—C(15)—C(16)	172.0(4)	C(1)—Si(1)—C(15)—C(16)	−167.9(3)
C(2)—Si(1)—C(15)—C(14)	−126.2(3)	C(2)—Si(1)—C(15)—C(14)	−108.0(3)
C(2)—Si(1)—C(15)—C(16)	53.4(5)	C(2)—Si(1)—C(15)—C(16)	70.4(4)
C(8)—Si(1)—C(15)—C(14)	114.1(3)	C(8)—Si(1)—C(15)—C(14)	131.4(3)
C(8)—Si(1)—C(15)—C(16)	−66.3(4)	C(8)—Si(1)—C(15)—C(16)	−50.1(4)
C(3)—Si(2)—C(1)—Si(1)	−67.1(3)	C(3)—Si(2)—C(1)—Si(1)	71.4(3)
C(3)—Si(2)—C(1)—Si(3)	66.8(3)	C(3)—Si(2)—C(1)—Si(3)	−60.9(3)
C(4)—Si(2)—C(1)—Si(1)	54.5(3)	C(4)—Si(2)—C(1)—Si(1)	−169.0(2)
C(4)—Si(2)—C(1)—Si(3)	−171.6(3)	C(4)—Si(2)—C(1)—Si(3)	58.6(3)
C(5)—Si(2)—C(1)—Si(1)	172.6(3)	C(5)—Si(2)—C(1)—Si(1)	−50.4(3)
C(5)—Si(2)—C(1)—Si(3)	−53.5(3)	C(5)—Si(2)—C(1)—Si(3)	177.2(2)
C(6)—Si(3)—C(1)—Si(1)	105.5(3)	C(6)—Si(3)—C(1)—Si(1)	139.3(2)
C(6)—Si(3)—C(1)—Si(2)	−34.3(3)	C(6)—Si(3)—C(1)—Si(2)	−82.5(3)
C(7)—Si(3)—C(1)—Si(1)	−129.1(2)	C(7)—Si(3)—C(1)—Si(1)	−95.5(2)
C(7)—Si(3)—C(1)—Si(2)	91.1(3)	C(7)—Si(3)—C(1)—Si(2)	42.7(3)
C(14)—Si(3)—C(1)—Si(1)	−11.9(3)	C(14)—Si(3)—C(1)—Si(1)	20.8(2)
C(14)—Si(3)—C(1)—Si(2)	−151.6(3)	C(14)—Si(3)—C(1)—Si(2)	159.0(2)
C(1)—Si(3)—C(14)—C(15)	8.0(4)	C(11)—Si(3)—C(14)—C(15)	−14.0(3)
C(1)—Si(3)—C(14)—C(19)	−173.0(4)	C(1)—Si(3)—C(14)—C(19)	167.1(3)
C(6)—Si(3)—C(14)—C(15)	−114.6(4)	C(6)—Si(3)—C(14)—C(15)	−133.3(3)
C(6)—Si(3)—C(14)—C(19)	64.4(5)	C(6)—Si(3)—C(14)—C(19)	47.8(4)
C(7)—Si(3)—C(14)—C(15)	125.8(4)	C(7)—Si(3)—C(14)—C(15)	106.0(3)
C(7)—Si(3)—C(14)—C(19)	−55.2(5)	C(7)—Si(3)—C(14)—C(19)	−72.9(4)

tion effects but not for absorption, and after averaging any equivalent reflections the 2127 unique reflections with $I > 3\sigma(I)$ based on counting statistics were used in the structure analysis.

The positions of the Si and C atoms were derived by direct methods and refined by full matrix least squares with anisotropic temperature factors to $R_F = 0.073$. The positions of the H atoms were taken from a difference map and included in further refinement with fixed positions and isotropic temperature factors equal to those of the C atom to which they are attached. The refinement finally converged at $R_F = 0.047$, $R_{\omega F} = 0.056$, where $\omega = 2.78/$

TABLE 3

DEVIATIONS (Å) OF ATOMS FROM VARIOUS MEAN PLANES. ATOMS NOT INCLUDED IN THE DERIVATION OF THE PLANES ARE MARKED †

Isomer A
1) C(14) 0.006, C(15) −0.001, C(16) 0.003, C(17) 0.002, C(18) −0.003,
    C(19) −0.005, Si(1) −0.004, Si(3) 0.002, C(1)† 0.246.
2) C(8) −0.005, C(9) 0.005, C(10) −0.001, C(11) −0.004, C(12) 0.004,
    C(13) 0.004, Si(1)† 0.006.
Angle between planes 1 and 2 is 83.3°.
Isomer B
3) C(14) 0.009, C(15) 0.011, C(16) −0.011, C(17) −0.002, C(18) 0.002,
    C(19) −0.001, Si(1) 0.001, Si(3) −0.009, C(1)† 0.425.
4) C(8) 0.005, C(9) 0.000, C(10) −0.010, C(11) 0.014, C(12) −0.007,
    C(13) 0.000, Si(1)† −0.050
Angle between planes 3 and 4 is 89.0°.

$[\sigma^2(F) + 0.0006F^2]$, with a maximum shift to error of 0.01. A final difference map was everywhere <0.2 eÅ^{-3}.

Isomer B

Crystal data: $C_{19}H_{28}Si_3$, MW = 340.7, triclinic, a 7.948(1), b 9.629(2), c 14.791(2) Å, α 96.92(2), β 95.75(2), γ 110.39(2)°, U 1041.0 Å^3, $Z = 2$, D_c 1.09 g cm^{-3}, $F(000) = 368$, Mo-K_α radiation, μ 2.2 cm^{-1}. Space group $P\bar{1}$.

The data crystal was an irregular shaped fragment of approximate size 0.4 × 0.3 × 0.3 mm. Data collection of $h \pm k \pm l$ reflections and processing were as for isomer A. The 2446 unique reflections with $I > 3\sigma(I)$ were used in the structure analysis.

The positions of the Si and C atoms were derived by the heavy atom procedure and refined by full matrix least squares with anisotropic temperature factors to $R_F = 0.084$. The positions of the H atoms were taken from a difference map and included in further refinement with fixed positions and isotropic temperature factors equal to those of the C atoms to which they are attached. The refinement converged at $R_F = 0.052$, $R_{\omega F} = 0.076$, where $\omega = 0.86/[\sigma^2(F) + 0.0039F^2]$, with a maximum shift to error of 0.3. A final difference map was everywhere <0.25 eÅ^{-3}.

For both structures the solution and refinement were done with the SHELX programme system of G.M. Sheldrick, and with scattering factors and dispersion corrections taken from ref. 11. Final atom positions are shown in Table 1(a) and 1(b) and other structural details in Tables 2 and 3. Tables of temperature factors, hydrogen atom parameters and structure factors can be obtained from the authors.

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