The reluctant titanium-catalyzed cyclotrimerization of 1-phenyl-2-(trimethylsilyl)acetylene. Crystal structure of 1,3,5-triphenyl-2,4,6-tris(trimethylsilyl)benzene

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Abstract

The cyclotrimerization of 1-phenyl-2-(trimethylsilyl)acetylene (PTMSA) catalyzed by the $TiCl_4/Et_2AlCl$ (Ti : Al = 10–20) system affords 1,3,5-triphenyl-2,4,6-tris(trimethylsilyl)benzene (I) (minor product) and ethyl-triphenyl-bis(trimethylsilyl)benzene (II) (major product) in low yields. An X-ray crystal structural study of I revealed that there are two different conformers in the unit cell. Compound I has a planar central ring with alternating values of angles at carbon atoms bearing the trimethylsilyl group (av. 116.8(6)°) and at carbon atoms bearing the Ph group (av. 123.1(9)°). The steric hindrance between the substituents is relieved by the almost perpendicular orientation of the Ph rings with respect to the central ring (81 ± 5°). The replacement of one trimethylsilyl group by an Et group from Et_2AlCl probably precedes the ring closure yielding II. The presence of trimethylsilyl groups on the carbon atoms involved in this step hinders the ring closure and gives rise to what are probably linear oligomers of PTMSA.

Key words: Titanium; Trimethylsilyl; Phenyl; Benzene; Catalysis; Crystal structure

1. Introduction

The cyclotrimerization of disubstituted acetylenes is known to be effectively catalyzed by a number of transition metal complexes [1–4] unless the formation of hexakis-substituted benzene is prevented by steric interaction of bulky substituents. A well known example of an unreactive acetylene is bis-trimethylsilyl)acetylene (BTMSA), which does not yield hexakis(tri-

methylsilyl)benzene although it does undergo catalyzed cycloaddition reactions [5,6]. This property of BTMSA enabled a highly selective preparation of 1,2-bis(trimethylsilyl)cyclohexa-1,4-diene derivatives by the [4 + 2] addition of BTMSA to conjugated dienes catalyzed by the $TiCl_4/Et_2AlCl$ system [7]. The phenyl substituents in diphenylacetylene (DPA) did not interfere with the easy cyclotrimerization in the presence of analogous titanium catalysts [8–11], but 1-phenyl-2-(trimethylsilyl)acetylene (PTMSA) was found to be unreactive [5]. Like BTMSA, PTMSA afforded [4 + 2] adducts with butadiene derivatives and the [6 + 2]

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adduct with 1,3,5-cycloheptatriene in high yields in the presence of the $TiCl_4/Et_2AlCl$ catalyst [12]. On the other hand, DPA gave only low yields of cross-adducts, affording mainly hexaphenylbenzene (HPB) [13]. In the absence of dienes or the triene, PTMSA gave a low yield of what were probably linear oligomers which, however, according to MS analysis contained a small amount of a cyclic PTMSA trimer [12].

We report here the structure of the low molecular cyclic products arising from the cyclotrimerization of PTMSA in the $TiCl_4/Et_2AlCl$/PTMSA/benzene system.

2. Experimental section

A high-vacuum technique, based on all-sealed devices and breakable seals, was used for introduction of catalyst components, PTMSA, and benzene. Benzene solutions of $TiCl_4$ and Et_2AlCl, PTMSA and benzene were identical with those used for the cross-addition reactions of PTMSA [12]. 1,2,4,5-Tetrakis(trimethylsilyl)benzene was prepared previously [14].

2.1. Instrumentation

Mass spectra were obtained on a JEOL JMS D-100 spectrometer at 75 eV using direct inlet. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 spectrometer (FT mode, 400 MHz for ^1H, 100 MHz for ^{13}C). Signal multiplicity in the ^{13}C NMR spectra was determined by the attached proton test (APT). Internal tetramethylsilane or the residual $CHCl_3$ signal were used for reference purposes. Infrared spectra of KBr pellets were recorded on a UR-75 spectrometer (Zeiss, Jena) in the region 400–3500 cm^{-1}.

2.2. Oligomerization of PTMSA

The reaction vessel was charged with benzene solutions of $TiCl_4$ (0.1 M, 1 ml) and Et_2AlCl (1.0 M, 1.5 ml) and the mixture was heated at 60°C for 10 min. It was then allowed to cool to room temperature and PTMSA (12.8 mmol, 2.5 ml) was added, the mixture was then heated again at 60°C for 3 h and then allowed to cool to ambient temperature. The ampoule was opened to air and the mixture transferred to a silica gel (L 100/160) column (length 7 cm) and eluted with a hexane-benzene (1:1) mixture and finally with benzene. Decomposition products of the catalyst remained trapped on the column. Solvents were removed from the eluates under reduced pressure; the yellow residues contained the products dissolved in unchanged PTMSA. This mixture was separated by liquid column chromatography on silica gel (length 25 cm) with hexane as eluent. The first fraction contained PTMSA, which was identified by GLC. The second fraction

yielded a white crystalline solid (110 mg, 4.6% based on consumed PTMSA) which was further separated into two components (denoted I and II) by crystallization from hexane. The less soluble compound I (15 mg) was obtained by repeated crystallization at $-20°C$ from concentrated hexane solutions; its purity in crystal fractions was checked by mass spectrometry. Compound II (40 mg) was isolated by cooling of the concentrated mother liquor after about half of the solute had crystallized out during slow evaporation of the hexane. The content of impurities was determined by mass spectrometry.

The yellow spot on the column was eluted by hexane-benzene mixtures with gradually increasing content of benzene. The solvents were evaporated to give a yellow wax residue (480 mg, 20%), which rapidly hardened in air. The fresh sample of the first fraction was sucked into the capillary for direct inlet injection in the mass spectrometer.

2.2.1. 1,3,5-Triphenyl-2,4,6-tris(trimethylsilyl)benzene (I)

M.p.: 223°C (223°C, ref. [5]). MS m/z (%): 523 ($M_i^{+\cdot}$; 8.1), 522 (M^+; 15.9), 508 (22.3), 507 (44.0), 491 (3.9), 475 (3.6), 459 (2.7), 449 (9.1), 435 (13.0), 434 (6.0), 433 (5.1), 419 (13.5), 403 (10.3), 361 (4.6), 347 (2.9), 345 (4.3), 159 (5.3), 135 (7.7), 73 (100), 45 (12.0); $m/2z$ (%): 246.5 (4.1), 246 (9.9), 238.5 (0.9), 238 (1.9), 230.5 (2.8), 230 (5.5), 222.5 (9.4), 222 (18.5); elemental composition of ions ($m/2z$, error in 10^{-3} of mass unit for ion): 246.1080 -1.7 for $C_{31}H_{36}Si_3^{2+}$, 222.0589 $+0.8$ for $C_{28}H_{24}Si_3^{2+}$.

IR (KBr pellet): 3100vw, 3078w, 3054w, 3024w, 2998w, 2952m, 2900m, 1600w, 1467m, br, 1445m, 1270m, 1253s, 1076w, 1025w, 879s, 855s, 840s, 821w, 775s, 760w, 714s, 680w, 630w, 559w, 473m cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 25°C): δ -0.531 (s, 27H, $SiMe_3$); 7.30–7.50 (mt, 15H, aromatic) ppm. ^{13}C NMR ($CDCl_3$, TMS, 25°C): δ 4.11 (q, 9C); 127.47 (d, 6C); 127.49 (d, 3C); 132.43 (d, 6C); 136.42 (s, 3C); 144.56 (s, 3C); 155.82 (s, 3C) ppm.

2.2.2. Ethyl-triphenyl-bis(trimethylsilyl)benzene (II)

M.p. 177°C. MS m/z (%): 479 ($M_i^{+\cdot}$; 8.7), 478 (M^+; 19.4), 466 (4.0), 465 (16.0), 464 (44), 463 (100), 447 (6.0), 431 (3.7), 389 (2.1), 375 (12.3), 345 (2.9), 224 (12.6), 216 (3.2), 135 (5.1), 73 (82), 59 (14.5); $m/2z$: 208, 208.5, 216, 216.5, 224, 224.5; elemental composition of ions (m/z, error in 10^{-3} of mass unit for ion): 463.2293 -1.5 for $C_{31}H_{35}Si_2^+$, 375.1548 $+2.1$ for $C_{27}H_{23}Si^+$, 224.1012 $+0.9$ for $C_{30}H_{32}Si_2^{2+}$, 135.0629 $+0.1$ for $C_8H_{11}Si^+$, 73.0477 -0.4 for $C_3H_9Si^+$.

IR (KBr pellet): 3100vw, 3080w, 3060w, 3023w, 2990w, 2966m, 2947sh, 2934w, 2900m, 2873w, 1601m,

1573w, 1510m, 1497m, 1450m, 1375m, 1255s, sh, 1160w, 1080m, 1053w, 1029m, 923w, 899s, 879s, 847vs sh, 783s sh, 713vs sh, 690s, 635m, 628m, 613m, 547w, 533w, 493w, 457w cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS, 25°C): δ $-$0.596 (s, 9H, SiMe$_3$); 0.063 (s, 9H, SiMe$_3$); 0.935 (t, 3H, CH$_3$CH$_2$, $J = 7.3$ Hz); 2.706 (q, 2H, CH$_3$CH$_2$); 7.077–7.436 (mt, 15H, aromatic) ppm. ^{13}C NMR (CDCl$_3$, TMS, 25°C): δ 3.33 (q, 3C); 3.81 (q, 3C); 17.09 (q); 27.75 (t); 125.63 (d); 126.01 (d); 126.41 (d, 2C); 126.90 (d, 2C); 127.52 (d); 127.58 (d, 2C); 131.00 (d, 2C); 131.83 (d, 2C); 132.33 (d, 2C); 134.56 (s); 136.53 (s); 139.88 (s); 141.09 (s); 143.02 (s); 146.02 (s); 149.37 (s); 149.85 (s); 155.86 (s) ppm. NMR spectra show the presence of two different SiMe$_3$ groups, three different phenyl groups and one Et group.

The composition of the yellow product was not studied in detail because it was not a single compound and was rapidly oxidized in air. The MS spectra of the first chromatographic fraction (evaporated in direct inlet up to 160°C) showed a sequence of ions of the general composition (n)A, $(n-1)$A + B, $(n-2)$A + 2B etc., where $n = 3$–5 and A denotes PTMSA and B phenylacetylene. These ions are accompanied by ions arising from elimination of Me group or H$_2$. The most abundant ion is m/z 73, SiMe$_3^+$. The product is apparently a mixture of linear oligomers of PTMSA that are partly deficient in SiMe$_3$ groups.

2.3. Treatment of 1,2,4,5-tetrakis(trimethylsilyl)benzene (TTMSB) with the TiCl$_4$/Et$_2$AlCl catalyst

The catalyst components were mixed and heated as described for the oligomerization of PTMSA. The heterogeneous mixture was added to 0.085 g of TTMSB under vacuum and subsequent treatment was as described above for PTMSA. The catalyst components were separated by chromatography on silica gel column (length 15 cm, eluted with hexane) and the colourless solution was evaporated to dryness. The mass spectra of the white finely crystalline solid showed the sole presence of TTMSB.

2.4. X-ray crystal structure analysis of I

A colourless cube-shaped crystal (0.3 × 0.3 × 0.25 mm) was mounted with epoxy glue on a glass fibre. The X-ray measurements were carried out on a Phillips PW1100 four-circle diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at room temperature. Crystal data for I: C$_{33}$H$_{42}$Si$_3$, M = 522.95, monoclinic, space group C2/c, a 44.971 (8), b 22.145 (4), c 12.543 (4) Å, β 95.14 (2)°, Z = 16, V = 12441 Å^3, D$_{calc}$ = 1.117 g cm^{-3}, μ = 1.35 cm^{-1}. Intensity data were collected by the $\theta/2\theta$ method: $2\theta_{max}$ = 44°. 6054 Reflections with $F_o > 1\sigma(F_o)$ out of 7177 unique observed reflections were used for further cal-

culations. The structure was solved by direct methods [15] and successive ΔF-syntheses. Two independent molecules, denoted I(1) and I(2), were found in the asymmetric unit. Unfortunately, the crystals were not transparent and their milky appearance indicated some internal imperfection. This is consistent with the relatively high R index and the unreliable positional parameters of C(132), yielding an unrealistic Si(13)–C(132) distance of 2.91(3) Å. Measurements with another crystal of approximately the same size did not give better results. The phenyl hydrogen atoms were included in calculated positions and methyl hydrogen atoms optimized on a cone. All non-hydrogen atoms were refined with anisotropic temperature factors. The final R indices with 653 parameters were R = 0.12 and R$_w$ = 0.14. The maximum residual electron density was 1 e/Å^3 at a distance of 0.6 Å from Si(13). The PC ULM package [16] was used for all the calculations. Atomic parameters for I(1) and I(2) are listed in Table 1. Selected bond distances and selected valence and torsion angles are given in Table 2 [17*].

3. Results and discussion

Treatment of PTMSA with the TiCl$_4$/Et$_2$AlCl system (mol. ratio PTMSA : Ti = 128) in benzene at 60°C for 3 h afforded a white solid product, moderately soluble in hexane, and a hexane-insoluble, yellow waxy product. The white product, obtained in only 4.6% yield based on consumed PTMSA, was resolved by fractional crystallization from hexane into two components, the less soluble compound I separating as colourless cube-shaped crystals and the more soluble compound II as a microcrystalline white powder. Both the compounds were characterized by m.p., MS, IR, ^{1}H and ^{13}C NMR spectra, and the X-ray single crystal structure was determined for I. The MS spectrum of I showed the molecular ion M$^{+\cdot}$ 522, corresponding to a PTMSA trimer. The NMR spectra revealed that I is the symmetrical cyclic trimer, with all the phenyl groups and all trimethylsilyl groups equivalent. Two different types of carbon atoms were in the central benzene ring. The symmetric structure of I was confirmed by an X-ray single crystal structural study (vide infra). Compound II yielded a mass spectrum with M$^{+\cdot}$ 478 and a fragmentation pattern consistent with the presence of one ethyl (Et) group instead of one trimethylsilyl group in the cyclic trimer. This assumption was confirmed by the NMR spectra, which showed the presence of one Et group, two different trimethylsilyl groups, and three

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* Reference number with asterisk indicates a note in the list of references.

different phenyl groups. Accordingly, all carbon atoms in the central benzene ring are non-equivalent. The MS analysis revealed that compound **II** contained < 1% of **I** and < 2% of a compound whose molecular ion corresponded to tetrakis(phenyl)-bis(trimethylsilyl)benzene, $(Ph)_4(SiMe_3)_2C_6$. The presence of these impurities and the propensity of **II** to form small crystalline aggregates prevented an X-ray diffraction study.

The ratio of **I** to **II** in their crude mixtures ranged from 1 : 10 to 1 : 20. This probably reflects the relative numbers of encounters of the first two PTMSA molecules leading to the initial formation of $=(Me_3Si)C-C(Ph)=$ and $=(Ph)C-C(Ph)=$ bonds, respectively. The latter case is apparently more favoured because of the absence of steric hindrance in this step. Addition of the third molecule of PTMSA to the latter dimeric intermediate is, however, sterically hindered, since a ring closure between two trimethylsilylated

TABLE 1. Atom coordinates and temperature factor for I(1) and I(2)

Atom	x	y	z	U_{eq}
Molecule I(1)				
C(11)	0.1261(2)	0.3191(3)	0.4457(6)	0.047(4)
Si(11)	0.1403(0)	0.2503(1)	0.3738(2)	0.063(1)
C(111)	0.1171(3)	0.1825(6)	0.3688(18)	0.209(20)
C(112)	0.1411(4)	0.2738(9)	0.2336(10)	0.164(14)
C(113)	0.1772(2)	0.2200(5)	0.4314(10)	0.104(8)
C(12)	0.1453(2)	0.3680(3)	0.4741(6)	0.048(4)
C(121)	0.1786(2)	0.3595(3)	0.4681(8)	0.057(5)
C(122)	0.1911(2)	0.3701(5)	0.3765(9)	0.085(7)
C(123)	0.2225(3)	0.3597(7)	0.3743(14)	0.123(11)
C(124)	0.2387(3)	0.3413(7)	0.4690(17)	0.127(13)
C(125)	0.2259(3)	0.3299(6)	0.5566(13)	0.110(10)
C(126)	0.1955(2)	0.3389(4)	0.5591(10)	0.084(7)
C(13)	0.1350(2)	0.4238(3)	0.5126(7)	0.059(5)
Si(13)	0.1618(1)	0.4888(2)	0.5456(6)	0.176(5)
C(131)	0.1488(2)	0.5634(4)	0.5595(10)	0.096(8)
C(132)	0.1701(5)	0.4760(9)	0.7776(38)	0.534(70)
C(133)	0.1992(2)	0.4841(5)	0.5449(13)	0.131(12)
C(14)	0.1046(2)	0.4288(3)	0.5235(7)	0.058(5)
C(141)	0.0925(2)	0.4889(4)	0.5560(10)	0.074(7)
C(142)	0.0943(2)	0.5060(4)	0.6615(10)	0.087(7)
C(143)	0.0839(3)	0.5612(5)	0.6935(10)	0.096(8)
C(144)	0.0699(3)	0.5983(5)	0.6179(12)	0.100(9)
C(145)	0.0678(2)	0.5817(4)	0.5127(11)	0.089(8)
C(146)	0.0790(2)	0.5270(4)	0.4821(9)	0.071(6)
C(15)	0.0838(2)	0.3808(3)	0.5022(7)	0.051(5)
Si(15)	0.0424(0)	0.3886(1)	0.5284(3)	0.074(2)
C(151)	0.0242(3)	0.3200(6)	0.5715(15)	0.157(14)
C(152)	0.0359(3)	0.4389(7)	0.6463(14)	0.155(14)
C(153)	0.0220(3)	0.4196(9)	0.4121(14)	0.175(16)
C(16)	0.0955(2)	0.3269(3)	0.4615(6)	0.046(4)
C(161)	0.0746(2)	0.2756(3)	0.4368(7)	0.052(5)
C(162)	0.0710(2)	0.2312(4)	0.5089(8)	0.073(6)
C(163)	0.0511(2)	0.1840(4)	0.4890(9)	0.088(7)
C(164)	0.0344(2)	0.1824(5)	0.3905(10)	0.083(7)
C(165)	0.0384(3)	0.2259(6)	0.3195(9)	0.102(8)
C(166)	0.0576(2)	0.2732(5)	0.3433(8)	0.078(6)

TABLE 1 (continued)

Atom	x	y	z	U_{eq}
Molecule I(2)				
C(21)	0.1332(2)	0.0639(3)	1.0957(6)	0.043(4)
Si(21)	0.1365(0)	−0.0105(1)	1.1766(2)	0.068(2)
C(211)	0.1692(2)	−0.0586(4)	1.1452(10)	0.100(8)
C(212)	0.1380(3)	0.0021(7)	1.3190(11)	0.134(11)
C(213)	0.1055(3)	−0.0670(5)	1.1477(12)	0.133(11)
C(22)	0.1592(2)	0.0972(3)	1.0780(6)	0.046(4)
C(221)	0.1894(2)	0.0729(3)	1.1242(8)	0.065(6)
C(222)	0.1978(2)	0.0780(4)	1.2300(9)	0.088(7)
C(223)	0.2246(3)	0.0544(6)	1.2721(12)	0.118(10)
C(224)	0.2436(3)	0.0287(7)	1.2018(21)	0.171(19)
C(225)	0.2345(3)	0.0222(7)	1.1026(18)	0.152(16)
C(226)	0.2073(2)	0.0454(4)	1.0581(10)	0.086(7)
C(23)	0.1585(2)	0.1499(3)	1.0169(6)	0.049(4)
Si(23)	0.1945(0)	0.1947(1)	0.9978(2)	0.068(2)
C(231)	0.2128(2)	0.1643(5)	0.8823(10)	0.105(9)
C(232)	0.1890(2)	0.2780(4)	0.9752(10)	0.093(8)
C(233)	0.2214(2)	0.1944(5)	1.1219(10)	0.105(8)
C(24)	0.1304(2)	0.1700(3)	0.9703(6)	0.046(4)
C(241)	0.1294(2)	0.2216(3)	0.8938(7)	0.051(5)
C(242)	0.1375(2)	0.2117(4)	0.7953(8)	0.066(6)
C(243)	0.1366(2)	0.2579(5)	0.7183(8)	0.081(7)
C(244)	0.1267(2)	0.3141(4)	0.7464(7)	0.069(6)
C(245)	0.1188(2)	0.3247(4)	0.8460(7)	0.063(5)
C(246)	0.1202(2)	0.2784(3)	0.9221(7)	0.056(5)
C(25)	0.1036(2)	0.1398(3)	0.9896(5)	0.041(4)
Si(25)	0.0655(0)	0.1733(1)	0.9369(2)	0.054(1)
C(251)	0.0564(2)	0.2360(5)	1.0285(9)	0.089(7)
C(252)	0.0323(2)	0.1235(4)	0.9274(10)	0.098(8)
C(253)	0.0643(2)	0.1989(5)	0.7970(8)	0.087(7)
C(26)	0.1062(1)	0.0882(3)	1.0531(6)	0.045(4)
C(261)	0.0781(1)	0.0571(3)	1.0841(6)	0.040(4)
C(262)	0.0645(2)	0.0140(3)	1.0158(7)	0.055(5)
C(263)	0.0391(2)	−0.0156(3)	1.0446(8)	0.060(5)
C(264)	0.0273(2)	−0.0028(4)	1.1382(8)	0.065(6)
C(265)	0.0411(2)	0.0398(5)	1.2033(9)	0.088(7)
C(266)	0.0659(2)	0.0705(4)	1.1767(7)	0.063(5)

carbon atoms is required. The absence of this step is proven by the absence of asymmetric cyclotrimers in the reaction products. As follows from the structure of major product **II**, the cyclotrimerization involving the more abundant dimeric intermediate is preceded by the replacement of one of the terminal trimethylsilyl groups by an Et group. The source of the Et group must lie in Et_2AlCl, which is present in 10–20-fold excess with respect to Ti. Such a process probably involves an ethyltitanium intermediate [18]. NMR spectroscopy did not distinguish between two possible isomers of **II**, 1-ethyl-3,4,6-triphenyl-2,5-bis(trimethylsilyl)benzene and 1-ethyl-3,5,6-triphenyl-2,4-bis(trimethylsilyl)benzene and hence it is impossible to specify whether the trimethylsilyl group was replaced by Et in the diene part or the acetylene part of a transient complex preceding the ring closure. Et–SiMe₃ exchange is unlikely in the asymmetric cyclic trimers of

TABLE 2. Selected bond distances (Å) and valence and torsion angles (°) for I(1) and I(2)

Molecule I(1)

C(11)–C(12)	1.409(10)	C(11)–Si(11)	1.908(8)
C(12)–C(13)	1.421(11)	C(12)–C(121)	1.516(11)
C(13)–C(14)	1.387(11)	C(13)–Si(13)	1.901(9)
C(14)–C(15)	1.426(11)	C(14)–C(141)	1.508(13)
C(15)–C(16)	1.417(10)	C(15)–Si(15)	1.927(8)
C(16)–C(11)	1.420(10)	C(16)–C(161)	1.491(10)
C(16)–C(11)–C(12)	116.8(6)	C(11)–C(12)–C(13)	122.9(7)
C(12)–C(13)–C(14)	117.2(7)	C(13)–C(14)–C(15)	123.8(7)
C(14)–C(15)–C(16)	115.9(7)	C(15)–C(16)–C(11)	123.3(7)
C(16)–C(11)–Si(11)	122.1(5)	C(12)–C(11)–Si(11)	120.7(5)
C(11)–C(12)–C(121)	118.4(6)	C(13)–C(12)–C(121)	118.6(7)
C(12)–C(13)–Si(13)	120.8(6)	C(14)–C(13)–Si(13)	121.9(6)
C(13)–C(14)–C(141)	118.7(7)	C(15)–C(14)–C(141)	117.4(7)
C(14)–C(15)–Si(15)	122.0(6)	C(16)–C(15)–Si(15)	122.1(5)
C(15)–C(16)–C(161)	118.0(6)	C(11)–C(16)–C(161)	118.7(6)

Torsion angles between the least square planes (°)
C(11) to C(16) and C(121) to C(126) 87.3
C(11) to C(16) and C(141) to C(146) 79.6
C(11) to C(16) and C(161) to C(166) 83.5

Molecule I(2)

C(21)–C(22)	1.416(10)	C(21)–Si(21)	1.935(7)
C(22)–C(23)	1.394(10)	C(22)–C(221)	1.528(11)
C(23)–C(24)	1.416(10)	C(23)–Si(23)	1.934(8)
C(24)–C(25)	1.419(10)	C(24)–C(241)	1.491(10)
C(25)–C(26)	1.392(10)	C(25)–Si(25)	1.928(7)
C(26)–C(21)	1.389(10)	C(26)–C(261)	1.522(9)
C(26)–C(21)–C(22)	116.3(6)	C(21)–C(22)–C(23)	123.0(7)
C(22)–C(23)–C(24)	117.7(7)	C(23)–C(24)–C(25)	121.5(6)
C(24)–C(25)–C(26)	117.0(6)	C(25)–C(26)–C(21)	124.3(6)
C(26)–C(21)–Si(21)	123.6(5)	C(22)–C(21)–Si(21)	120.0(5)
C(21)–C(22)–C(221)	118.4(6)	C(23)–C(22)–C(221)	118.6(7)
C(22)–C(23)–Si(23)	121.3(5)	C(24)–C(23)–Si(23)	121.0(5)
C(23)–C(24)–C(241)	118.8(6)	C(25)–C(24)–C(241)	119.6(6)
C(24)–C(25)–Si(25)	120.2(5)	C(26)–C(25)–Si(25)	122.7(5)
C(25)–C(26)–C(261)	119.1(6)	C(21)–C(26)–C(261)	116.5(6)

Torsion angles between the least square planes (°)
C(21) to C(26) and C(221) to C(226) 73.9
C(21) to C(26) and C(241) to C(246) 76.0
C(21) to C(26) and C(261) to C(266) 84.7

PTMSA because no such reaction was observed for 1,2,4,5-tetrakis(trimethylsilyl)benzene.

The yellow hexane-insoluble product is probably a mixture of linear oligomers that are very sensitive to oxidation by air. The oxidation is demonstrated by rapid hardening of the waxy product and by appearance of the absorption band of ν(C=O) vibrations above 1600 cm^{-1}. The linear oligomers can be formed from the dimeric intermediate leading to **II**, which, however, avoids the SiMe$_3$–Et exchange followed by the ring closure. The mass spectra of the fraction of low molecular oligomers (up to pentamer) showed, in addition to ions corresponding to oligomers of PTMSA, very abundant ions formed by the loss of silabutylene

and silabutylene and one hydrogen molecule. These eliminations can occur upon electron impact on the normal oligomer of PTMSA or even during the oligomerization process in order to release steric hindrance in a catalytically active titanium complex.

The crystal structure of **I** is noteworthy in that it is intermediate between structures of hexaphenylbenzene **(III)** [19] and hexakis(trimethylsilyl)benzene **(IV)** [20]. The asymmetric unit cell contains two molecules in different conformations, denoted by I(1) and I(2). The molecular structures of both molecules are shown in Fig. 1.
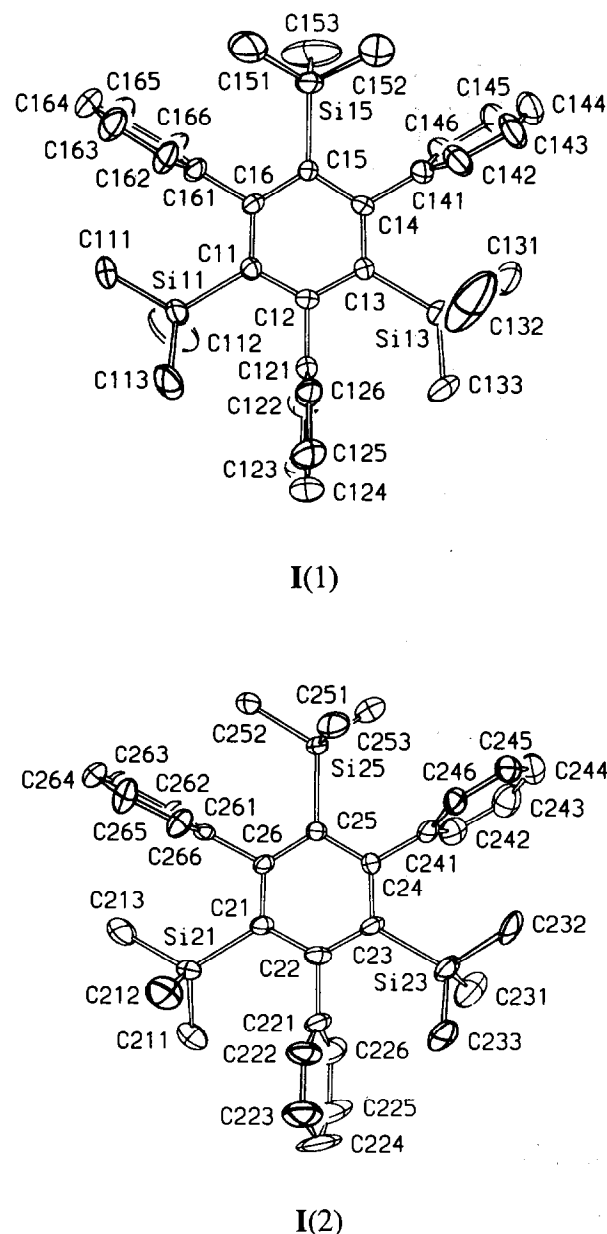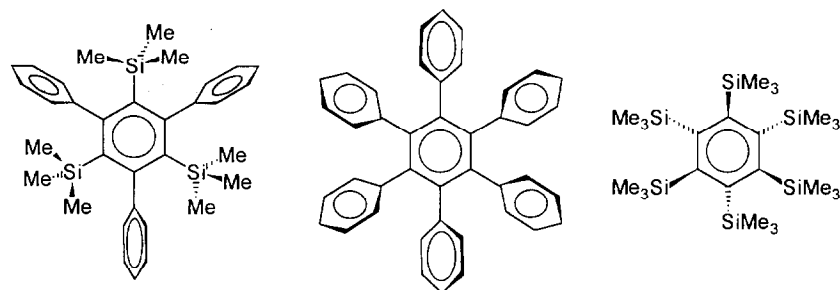

I(1)

I(2)

Fig. 1. The molecular structure and atom numbering scheme for I(1) and I(2).

1,3,5-triphenyl-2,4,6-tris-   hexaphenylbenzene (III)   hexakis(trimethylsilyl)benzene (IV)
(trimethylsilyl)benzene (I)

Fig. 2. Schematic structures of the crowded benzene derivatives.

The effect of steric strain on the geometry of benzene derivatives I, III, and IV is depicted in Fig. 2. In each of the three molecules the steric strain imposed by the bulky substituents is released in a different way. The trimethylsilyl groups in IV lie alternately by on average 0.94(3) Å above and below the least square plane formed by the ring carbon atoms. The maximum deviation (md) of the ring atoms from their least square plane is 0.05 Å, the average deviation (ad) is 0.04 Å [20,21*]. The central benzene ring is slightly bent in a manner matching the deviations of the trimethylsilyl groups. The central benzene ring in III is closer to planar (md = 0.03 Å, ad = 0.01 Å) and the mutual steric repulsion of phenyl rings is responsible for a propeller-like arrangement of the phenyl substituents. The torsion angles between the central benzene ring and the phenyl rings range from 62.2° to 70.7° (average 67 ± 3°) [19,21].

The structure of I is determined by the interaction between the trimethylsilyl and phenyl groups, and differs remarkably from those of III and IV. The central benzene ring of I is effectively planar (md = 0.02 Å,

ad = 0.01 Å for I(1) and md = 0.03 Å, ad = 0.02 Å for I(2)), and the maximum deviation of the pivotal C atoms of phenyl substituents and Si atoms from this plane is only 0.3 Å (av. 0.1 Å). The steric hindrance between the trimethylsilyl and phenyl groups results in the nearly perpendicular orientation of phenyl rings with respect to the central ring (73.9–87.3°, av. 81 ± 5°). Moreover, the steric strain is released by the in-plane distortion of the central ring: the angles at the (2,4,6-) carbon atoms bearing the trimethylsilyl group are significantly smaller (av. 116.8(6)°) than those at the (1,3,5-) carbon atoms bearing the phenyl groups (av. 123.1(9)°). The corresponding exocyclic angles at the 2,4,6-carbon atoms are correspondingly larger than those at the 1,3,5-carbon atoms. Close contacts between the carbon atoms of methyl groups and carbon atoms of phenyl rings are given in Table 3. These distances are significantly shorter than the interlayer distance in graphite (3.354 Å) [22] although the presence of hydrogen atoms in I was not taken into account. Common structural features of I, III and IV are summarized in Table 4.

The steric strain in I is probably reflected in the mass spectral fragmentation, which is characterized by easy elimination of the methyl radical, followed by up to three molecules of methane, and by the trimethylsilyl radical. The fragmentation of the less crowded II is, however, very similar.

TABLE 3. Close contacts between carbon atoms of the trimethylsilyl and phenyl substituents in I

Molecule I(1)			
C(111)–C(161)	2.986(18)	C(111)–C(162)	3.032(19)
C(113)–C(121)	3.123(14)	C(113)–C(126)	3.154(15)
C(131)–C(141)	3.022(15)	C(131)–C(142)	3.134(15)
C(133)–C(121)	3.042(15)	C(133)–C(122)	3.291(17)
C(151)–C(161)	3.105(17)	C(151)–C(162)	3.035(18)
C(152)–C(141)	3.083(19)	C(152)–C(142)	3.012(19)
Molecule I(2)			
C(211)–C(221)	3.071(14)	C(211)–C(226)	3.127(15)
C(213)–C(261)	3.089(14)	C(213)–C(262)	2.971(15)
C(232)–C(241)	3.050(13)	C(232)–C(246)	3.106(13)
C(233)–C(221)	3.051(14)	C(233)–C(222)	3.141(15)
C(252)–C(261)	3.089(12)	C(252)–C(262)	2.985(13)
C(253)–C(241)	3.108(12)	C(253)–C(242)	3.307(13)

TABLE 4. Comparison of average bond distances in I, III and IV (C(ce)—carbon atom of the central benzene ring)

	I	III [a]	IV
C(ce)–C(ce)	1.41(1)	1.40(1)	1.41
C(ce)–C(Ph)	1.51(1)	1.50(2)	–
C(ce)–Si	1.92(1)	–	1.92
C(Ph)–C(Ph)	1.37(3)	1.40(2)	–
Si–C(Me)	1.84(5) [b]	–	1.87

[a] Values calculated from the data of ref. [19] using [16]. [b] Bond distance Si(13)–C(132) was ignored (vide supra).

In the infrared spectra, no effect of steric strain on the frequency of ν(C–H) vibration [23] was observed, but changes in their intensities compared to similar compounds are noteworthy; *e.g.*, the order of ν(C–H) intensities in **I** (2998 ~ 3055 > 3024 ~ 3078 > 3100 cm^{-1}) differs from that in hexaphenylbenzene (3027 > 3057 > 3081 > 3102 ~ 2998 cm^{-1} [11]). The intensities of the characteristic ν(C–H) vibrations of SiMe$_3$ group for **I** (2900 > 2950 cm^{-1}) are the reverse of those for 1-phenyl-2-trimethylsilylbenzene [12] and 1,2,4,5-tetrakis(trimethylsilyl)benzene [14].

Acknowledgments

References

1 M.J. Winter, Alkyne oligomerization, in F.R. Hartley and S. Patai (eds.), *The Chemistry of the Metal–Carbon Bond. Carbon–Carbon Bond Formation Using Organometallic Compounds*, Wiley, Chichester, 1985, Vol. 3, Chapter 5.

2 P.M. Maitlis, *J. Organomet. Chem., 200* (1980) 161.

3 S. Otsuka and A. Nakamura, *Adv. Organomet. Chem., 14* (1976) 245.

4 N.E. Schore, *Chem. Rev., 88* (1988) 1081.

5 U. Krüerke and W. Hübel, *Chem. Ber., 94* (1961) 2829.

6 K.P.C. Vollhardt, *Acc. Chem. Res., 10* (1977) 1.

7 K. Mach, H. Antropiusová, L. Petrusová, F. Tureček, V. Hanuš, P. Sedmera and J. Schraml, *J. Organomet. Chem., 289* (1985) 331.

8 E.F. Lutz, *J. Am. Chem. Soc., 83* (1961) 2551.

9 A.F. Donda, E. Cervone and M.A. Biancifiori, *Recl. Trav. Chim. Pays-Bas, 81* (1962) 585.

10 G. Drefahl, H.H. Hörhold and H. Bretschneider, *J. Prakt. Chem., 25* (1964) 113.

11 F. Calderazzo, F. Marchetti, G. Pampaloni, W. Hiller, H. Antropiusová and K. Mach, *Chem. Ber., 122* (1989) 2229.

12 R. Klein, P. Sedmera, J. Čejka and K. Mach, *J. Organomet. Chem., 436* (1992) 143.

13 K. Mach, H. Antropiusová, P. Sedmera, V. Hanuš and F. Tureček, *J. Chem. Soc., Chem. Commun.*, (1983) 805; K. Mach, H. Antropiusová, L. Petrusová, V. Hanuš, F. Tureček and P. Sedmera, *Tetrahedron, 40* (1984) 3295.

14 K. Mach, F. Tureček, H. Antropiusová and V. Hanuš, *Organometallics, 5* (1986) 1215.

15 G. Sheldrick, SHELXS Program system, Crystallographic Computing 3, Oxford University Press, 1985.

16 R. Brüggemann, T. Debaerdemaeker, B. Müller, G. Schmid and U. Thewalt, *Z. Kristallogr., 5* (1992) 33.

17 Further details concerning the crystal structure analysis are available upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the deposition number CSD-57502, the name of the author, and the journal citation.

18 J. Boor, Jr., *Ziegler-Natta Catalysts and Polymerization*, Academic Press, New York, 1979, p. 670.

19 J.C.J. Bart, *Acta Cryst., B 24* (1968) 1277.

20 H. Sakurai, K. Ebata, C. Kabuto and A. Sekiguchi, *J. Am. Chem. Soc., 112* (1990) 1799.

21 Values calculated from literature data using PC ULM package [ref. 16].

22 J. Donohue, *The Structure of the Elements*, John Wiley, New York, 1974, p. 250.

23 E.M. Arnett and J.M. Bollinger, *J. Am. Chem. Soc., 86* (1964) 4729.