Discussion

The conformation of the COT carbon atoms could be related to the rotamer angle which was defined previously. Thus tub and folded ring stereochemistries are expected for rotamer angles of 22.5 and 0°, respectively. Despite the fact that the rotamer (12.7°) found in molecule 1 is more like the former while that (9.9°) of molecule 2 most closely resembles the latter, it is not understandable why a small change in conformation angle (3°) leads to such a large difference in ring stereochemistry.

Asymmetric π bonding of other carbocyclic ligands to metal atoms has been detected previously,[7] but the interesting feature of the (COT)Zr systems is the larger degree of flexibility in this linkage. While the effects of steric repulsions on the Zr–C(COT) bond distances are difficult to dismiss, we feel that the following electronic factors merit attention. Consider a coordinate system on the Zr atom with z along the COT plane normal, y along the normal to the C(10)–Zr–O plane, and x chosen to complete a right-handed framework. The interaction of the allyl fragment and alkoxy group with the Zr atom will lift the degeneracy of the $4d_{xz}$ and $4d_{yz}$ orbitals, forcing the former to higher energy. Now an important part of the COT–Zr bonding will be the interaction of the ring e_1 orbitals with the higher lying $4d_{xz}$ and $4d_{yz}$ functions of the metal atom.[8] Since the energy difference between the ring orbital and $4d_{xz}$ will be greater than that involving $4d_{yz}$, the latter interaction will be stronger. In other words, the shorter Zr–C(COT) bonds should be those most nearly perpendicular to the C(10)→O vector. This is observed.

Registry No. I, 79703-91-6.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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Stereochemistry of Transition Metal Cyclooctatetraenyl Complexes. Molecular Structure of (η-Cyclooctatetraenyl)(η^3,$\eta^{3'}$-deca-2,7-diene-4,9-diyl)zirconium

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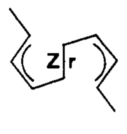
(η-Cyclooctatetraenyl)(η^3,$\eta^{3'}$-deca-2,7-diene-4,9-diyl)zirconium crystallizes in the space group $P2_1/n$ with a = 12.646 (4) Å, b = 14.185 (4) Å, c = 8.373 (2) Å, β = 95.89 (2)°, d_{calcd} = 1.474 g/cm^3, and Z = 4. Least-squares refinement of the structure converged with a conventional R value of 0.020 for 3506 counter-measured X-ray data with $I > 2\sigma(I)$. The monomeric molecules have approximate C_2 symmetry. Highly asymmetric Zr–allyl bonding is found. The Zr–C(allyl) distances average 2.385 (6), 2.532 (3), and 2.824 (2) Å, the longest and shortest distances being associated with methyl- and methylene-substituted carbon atoms, respectively. While the former pair displays trigonal hydridization, the stereochemistry of the latter pair is more nearly tetrahedral. The reason for the asymmetrical bonding is traced to the relief of nonbonded repulsion between the zirconium and methylene carbon atoms. The Zr–C(COT) bond distances display significant variations which cannot be traced to a trans effect induced by the asymmetrical Zr–allyl bonding but rather to steric repulsion between the two hydrocarbyl ligands. On the average, the C–H vectors of the COT ligand are tilted 6.1 (9)° out of the COT carbon atom plane toward the metal atom.

Introduction

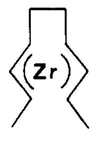
While $Zr(C_3H_5)_4$ catalytically converts butadiene into low molecular weight polybutadienes,[1] the catalytic oligomerization of butadiene by (η-COT)$Zr(C_3H_5)_2$ (I), COT = 1,3,5,7-cyclooctatetraene, yields mainly the dimer octa-1,3,6-triene and only traces of higher polymers.[2] This contrast in product distributions suggests that the (COT)Zr fragment remains intact during the latter reaction. Indeed, the isolation of an intermediate (II) was reported which contained a butadiene dimer attached via two allyl fragments to a (η-COT)Zr moiety.[2] IR and NMR investigations of II suggested an asymmetric π-allyl-bonding mode with terminal C atoms being further from the Zr atom than those C atoms adjacent to the C–C bond joining the two butadiene species.[2]

The catalytic polymerization of *cis*-piperylene by I is more complex. In addition to lesser amounts of higher oligomerics, mixtures of 4-nonatrienes and decatrienes were obtained. Intermediates were also detected by NMR in this case, the one containing a C_{10} chain (III) being isolated. According to the NMR results, III would correspond to a 1,8-dimethyl derivative of II,[3] that is, (η-COT)(η^3-$CH_3CHCHCHCH_2)_2Zr$.

An X-ray structural study on III appeared desirable. First, establishment of the C_{10} chain symmetry, both C_s (A) and C_2 (B) geometries being compatible with the



A



B

spectroscopic data, might help clarify the mechanism of hydrogen transfer occurring during displacement of the

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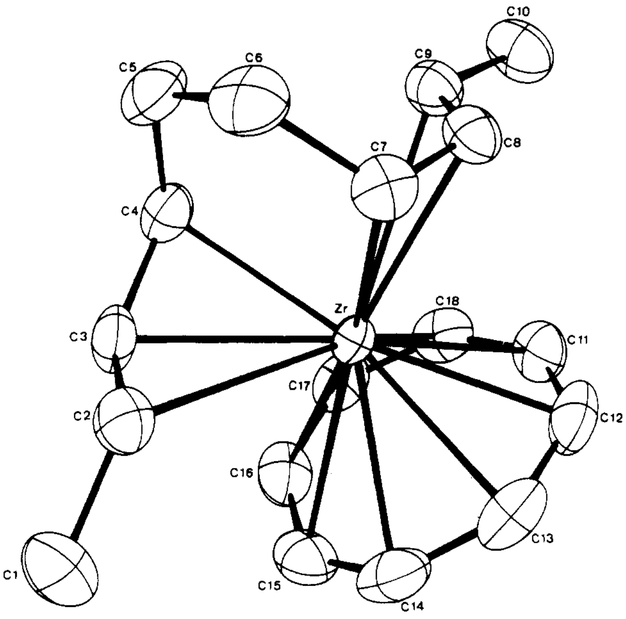

Figure 1. A perspective drawing of III with hydrogen atoms omitted.

piperylene dimer from the Zr coordination sphere. Second, while structural details of the symmetric (π-C_3H_5)Zr fragment in (η-COT)(π-C_3H_5)$ZrOC_4H_9$ (IV)[4] are available, corresponding asymmetric linkages have not been studied. Third, in connection with our previous studies[4-6] of the (η-COT)Zr stereochemistry, detection of asymmetry in this fragment which might be induced by the (π-allyl)$_2$Zr interaction is of general interest.

Experimental Section

Crystals of III, which were kindly supplied by Dr. H.-J. Kablitz of this institute, were mounted in glass capillaries under argon. The space group $P2_1/n$ was determined from Weissenberg photographs. Cell constants, obtained from θ values measured on a CAD-4 diffractometer employing graphite-monochromatized Mo K$\bar{\alpha}$ (λ = 0.71069 Å) radiation, are a = 12.646 (4) Å, b = 14.185 (4) Å, c = 8.373 (2) Å, β = 95.89 (2)°, d_{calcd} = 1.474 g/cm^3 and Z = 4.

Two forms (hkl, $\bar{h}kl$, $h\bar{k}l$, $\bar{h}\bar{k}l$, 1° < $\theta \leq$ 30°) of data were measured by the multispeed ω–2 θ scan technique as described previously.[7] No indication of crystal or diffractometer instability was obtained by periodically monitoring of three standard reflections during the course of data collection. The data were corrected for absorption, converted to $|F_o|$'s, and merged. Of the 8729 reflections measured, the 3506 unique data with $I \geq 2\sigma(I)$ were deemed observed and 861 were unique and were unobserved. Only observed reflections were assigned nonzero weights and included in the solution and refinement of the structure.

The structure was solved by the heavy-atom method and refined by large-block least-squares techniques using previously published procedures.[6] After anisotropic refinement of all C atoms, the H atoms were located with a difference Fourier synthesis and subsequently refined isotropically. Refinement converged with $R = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.020 and $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$ = 0.022. The final positional parameters are given in Table I. The numbering scheme is defined in Figure 1, the H atoms being numbered after the C atoms to which they bond.

Description of the Crystal Structure

Crystals of III are formed from discrete molecules separated by van der Waals contacts. While no crystallographic symmetry is imposed on the molecules, the molecular symmetry is approximately C_2, the two fold axis bisecting C(5)–C(6) and passing through the zirconium atom. Accordingly, averaged structural parameters are mentioned in the text. (Standard deviations are taken as the larger of $[\sum_{i=1}^{n}(p_i - \bar{p})^2/n(n-1)]^{1/2}$ and $(\sum_{i=1}^{n}\sigma_i^2)^{1/2}/n$, where σ_i is derived from the errors quoted in Table I.) The thermal parameters of the zirconium and COT carbon atoms can be approximated by a rigid-body-motion model.[8] Librational corrections to the corresponding Zr–C and C–C bond lengths were found to be small but significant. Unless designated to the contrary, only uncorrected distances are mentioned in the text. The validity of the H atom refinement may be judged by the low root-mean-square variation, 0.03 Å, mean C–H distance 0.95 Å.

Table I. Final Atomic Coordinates and Their Standard Deviations (×10^5)

atom	x	y	z
Zr	968 (1)	2033 (1)	1417 (1)
C(1)	1068 (2)	3957 (1)	−1940 (2)
C(2)	1465 (1)	3020 (1)	−1338 (2)
C(3)	885 (1)	2217 (1)	−1598 (2)
C(4)	1196 (1)	1283 (1)	−1065 (2)
C(5)	2299 (1)	911 (1)	−1286 (2)
C(6)	3177 (1)	1384 (1)	−204 (2)
C(7)	2815 (1)	1682 (1)	1395 (2)
C(8)	2504 (1)	1000 (1)	2529 (2)
C(9)	1844 (1)	246 (1)	2251 (2)
C(10)	1560 (1)	−399 (1)	3552 (2)
C(11)	387 (1)	1713 (1)	4179 (2)
C(12)	1057 (1)	2504 (1)	4307 (2)
C(13)	1136 (1)	3319 (1)	3411 (2)
C(14)	525 (1)	3687 (1)	2073 (2)
C(15)	−365 (1)	3384 (1)	1066 (2)
C(16)	−927 (1)	2544 (1)	804 (2)
C(17)	−925 (1)	1674 (1)	1582 (2)
C(18)	−382 (1)	1343 (1)	3018 (2)
H(1A)	1246 (16)	4453 (14)	−1338 (26)
H(1B)	1446 (24)	4115 (24)	−2826 (37)
H(1C)	297 (17)	3991 (16)	−2239 (25)
H(2)	2199 (15)	2943 (11)	−875 (23)
H(3)	187 (14)	2307 (13)	−2003 (21)
H(4)	594 (12)	820 (12)	−1309 (18)
H(5A)	2278 (15)	269 (13)	−1116 (24)
H(5B)	2450 (13)	986 (12)	−2405 (20)
H(6A)	3795 (16)	987 (17)	−37 (25)
H(6B)	3492 (15)	1939 (11)	−647 (22)
H(7)	3223 (16)	2172 (13)	1970 (24)
H(8)	2640 (13)	1131 (12)	3708 (20)
H(9)	1617 (11)	33 (12)	1179 (17)
H(10A)	1752 (15)	−101 (15)	4552 (25)
H(10B)	822 (17)	−500 (16)	3486 (28)
H(10C)	1970 (19)	−954 (18)	3491 (29)
H(11)	607 (14)	1212 (13)	4940 (21)
H(12)	1644 (18)	2479 (17)	5172 (27)
H(13)	1715 (15)	3686 (13)	3864 (24)
H(14)	789 (17)	4273 (17)	1717 (25)
H(15)	−493 (15)	3819 (15)	209 (23)
H(16)	−1358 (20)	2544 (21)	−177 (32)
H(17)	−1398 (16)	1244 (14)	1136 (24)
H(18)	−498 (14)	708 (14)	3173 (22)

Two allyl fragments of the C_{10} chain are bonded to the zirconium atom. Rather than possessing two sets of three nearly equal Zr–C(allyl) separations of about 2.50 Å as in IV,[4] the distances in III vary from 2.385 (6) to 2.824 (2) Å. The shortest bonds involve the carbon atoms adjacent to the ethylene bridge and indicate a strong bonding interaction. The longest distances suggest at most very weak bonding, but a similarly long Zr–C contact was found in the Zr(butadiene) fragment of (η^8-COT)(η^4-COT)Zr·THF.[5]

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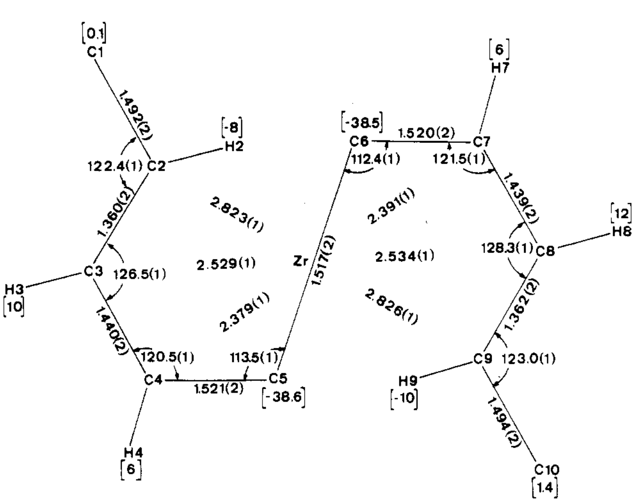

Figure 2. Important distances (Å) and angles (deg) in the diallyl zirconium fragment including angles formed by the allyl substituents with the allyl planes in brackets. A positive sign for the latter angles indicates an inclination toward the metal atom.

As would be expected for a highly asymmetrically bonding π-allyl moiety, bonds between the pairs of carbon atoms closest to the zirconium atom are distinctly longer (1.440 (1) Å) than those between the other pair (1.361 (1) Å).

The methyl and methylene allyl substituents occupy syn and anti positions, respectively. While the methyl carbon atoms lie essentially in the allyl carbon atom planes, the methylene carbon atoms lie 0.94 Å above the planes away from the zirconium atom (Figure 2). The direction of H(meso), H(syn), and H(anti) displacements from the allyl planes in III are the same as those in IV, but the degree of hydrogen nonplanarity in III is only about half of that in IV.[4] Evidence for steric strain in the C_{10} chain conformation is offered by the C(4)–C(5)–C(6)–C(7) torsion angle of 32.0°, which is midway between eclipsed and staggered values.

Although COT is clearly η^8 bonded to the zirconium atom, the Zr–C(COT) bond lengths deviate significantly and systematically (Figure 3) from their mean value (2.499 Å, corrected 2.511 Å). Deviations of the COT carbon atoms from coplanarity are present which are as large as 0.1 Å, and the pattern of nonplanarity correlates with the Zr–C(COT) distances (Figure 3). Similar though smaller deviations from C_{8v} symmetry were found for the (η-COT)Zr entities in IV[4] and (η-COT)$ZrCl_2$·THF[6] and were attributed to electronic and/or steric perturbations introduced by the other zirconium ligands.

In III, the strongest Zr–allyl interactions are approximately trans to the shortest Zr–COT distances (Figure 4); therefore, the variation in these bond lengths cannot be attributed to a normal trans influence. Indication of important steric effects has been found. Nonbonded contacts as short or shorter than respective sums of van der Waals radii (C–C = 3.40 Å; C–H = 2.90 Å; H–H = 2.40 Å) are shown in Figure 4. The crowding at C(11) and C(15), the carbon atoms farthest from the zirconium atom, is obvious. In addition, the repulsive contacts C(8)–C(12) and C(3)–C(16) are shorter than C(9)–C(18) and C(2)–C(14), and Zr–C(12) and Zr–C(16) are significantly longer than Zr–C(18) and Zr–C(14). The C–C distances in the COT ring average 1.398 (2) Å, corrected 1.407 (2) Å.

When projected on the normal to the COT carbon atom best plane, each COT hydrogen atom is closer to the zirconium atom than is the carbon atom to which it is attached. The average out of plant tilt angle is defined by the complement (Figure 3) of the mean angle formed by the C–H vectors with the COT carbon atom plane normal, 6.1 (9)°, and compares well with previous observations.[4,6]

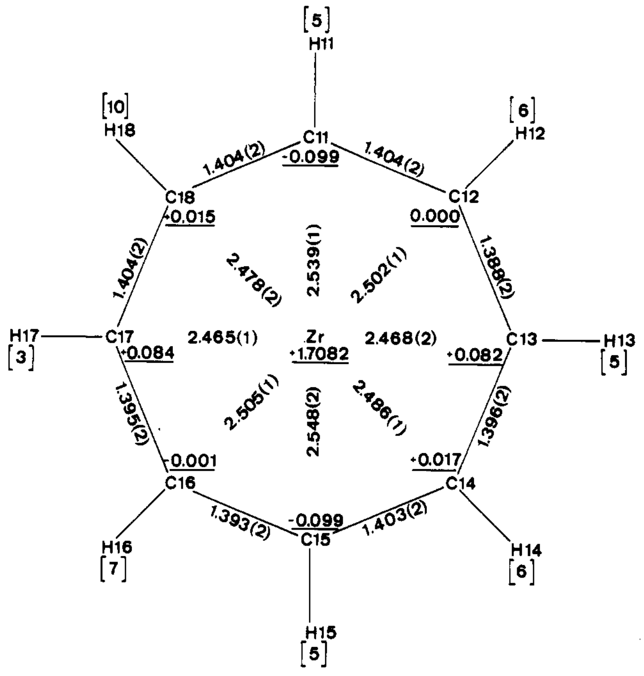

Figure 3. Selected bond distances and deviations (underscored) from the COT carbon atom best plane (Å) as well as angles (deg) formed by C–H vectors with the COT plane in brackets.

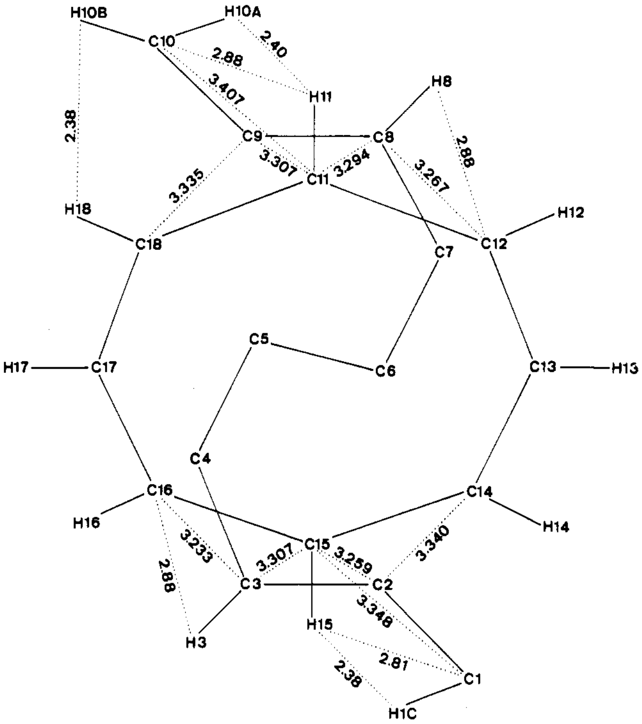

Figure 4. Repulsive nonbonded contacts (dotted lines, Å) between the COT and diallyl ligands.

Discussion

Bonded to one COT ligand and two allyl fragments, the zirconium atom in III obtains an 18-electron, inert-gas configuration. Since no obvious electronic factors would favor asymmetric allyl linkages in this case, steric influences may be responsible for the observed distortions. The most serious steric constraint is the $-CH_2-CH_2-$ bridge joining the two allyl fragments. Due to the twofold symmetry, the bridging carbon atoms are brought closer to the zirconium atom than would be required by their anti positions with respect to the allyl fragments. To lengthen these contacts, the methylene groups move out of the allyl planes away from the Zr atom. This means that the hybridization of C(4) and C(7) changes from sp^2 to sp^3 with consequential change from π to σ Zr–C(4) and Zr–C(7) bonding. Indeed these bond lengths lie in the range of other σ Zr–C bonds.[9]

The prediction[2] of the type of Zr–allyl asymmetry in II is particularly important. The distortions could be caused by the repulsions just described for the case in III if the C_8 chain also has C_2 symmetry. This conformation is of particular interest since it brings a bridging methylene group of one butadiene fragment into the proximity of the terminal methylene group of the other. Upon displacement of the dimer from the complex, H transfer occurs from the former to the latter group forming octa-1,3,6-triene.[2] Correspondingly, the product mixture obtained by catalytically oligomerizing piperylene with I contains deca-2,4,7-triene; therefore, III appears to be a true intermediate.[3]

As C(2) and C(9) are far from the zirconium atom, coplanarity of the methyl carbon atoms with the respective allyl fragments might mean that C(2) and C(9) do not interact with the zirconium atom. However, H(2) and H(9) are not coplanar with the allyl moieties and thus indicate stereochemically significant Zr–C(2) and Zr–C(9) bonding. A possible explanation for these contradictory observations is as follows. A normal Zr–allyl interaction is accompanied by C–H(syn) and C–H(meso) bonds inclining out of the allyl plane toward the Zr atom while C–H(anti) bonds bend in the opposite direction.[4] These departures from planarity, which probably signalize the mixing of carbon σ and π orbitals, tend to lengthen the nonbonded contacts Zr–H(anti) while Zr–H(syn) and Zr–H(meso) tend to shorten. Therefore exactly opposite to the above-described case of anti substitution by a methylene group, syn substitution by the sterically larger methyl group should oppose nonplanarity and the subsequent increase in Zr–CH$_3$ nonbonded repulsions.

Registry No. III, 79681-74-6.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Communications

Thermochemistry of Di- and Trisilanyl Radicals. Observations and Comments on Silene-to-Silylene Rearrangements

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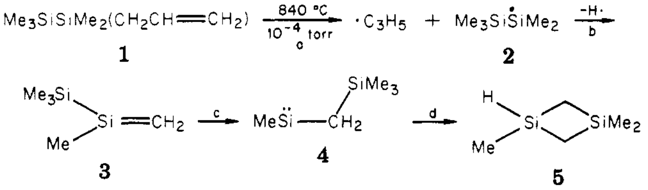
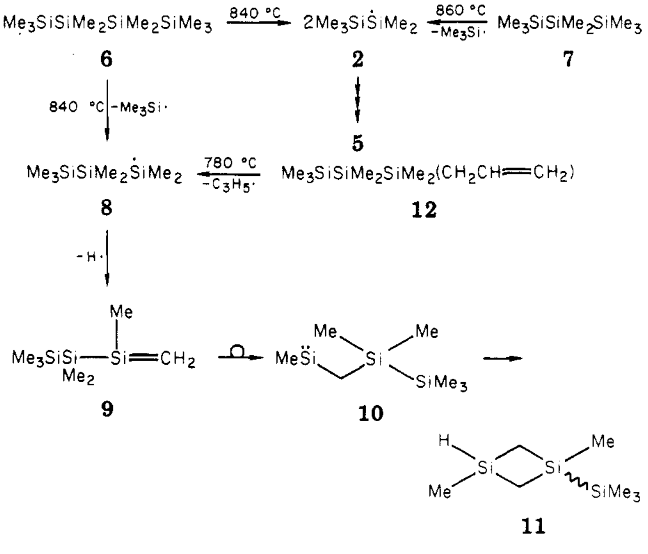
Summary: Di- and trisilanyl radicals are shown to undergo a thermal sequence of disproportionation to silenes, rearrangement to silylenes via 1,2-silyl migration, and cyclization via γ-C–H insertion.

Recently we reported[1] that flash vacuum pyrolysis of allylpentamethyldisilane (1) gave rise to 1,1,3-trimethyl-1,3-disilacyclobutane (5) as the major volatile product. Our proposed mechanism consisted of four steps: (a) Si–C bond homolysis to form pentamethyldisilanyl radical (2); (b) disproportionation of 2 to form silylsilene 3; (c) rearrangement of 3, via 1,2 migration of Me$_3$Si–, to β-silylsilylene 4; and (d) γ-CH insertion by 4 to form 5. Although steps a,[2] b,[3] and d[4] have literature precedents, step c had never before been observed or postulated.



One of the experimental necessities to establish the disproportionation of 2 to 3 was to explain the absence of decamethyltetrasilane (6), the expected radical combination product of 2. Thus, we conducted the flash vacuum pyrolysis of 6 under the conditions employed for 1 (840 °C, 10^{-4} torr; horizontal quartz-packed tube). Indeed the major volatile product of this pyrolysis is 5 (21%), which



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