Table V. Selected Bond Distances (Å) and Angles (deg) for 5

Distances

Mo–C(10)	1.95 (2)	C(10)–O(1)	1.15 (1)
Mo–C(20)	1.94 (2)	C(20)–O(2)	1.16 (1)
Mo–C(30)	1.93 (2)	C(30)–O(3)	1.17 (1)
Mo–C(1)	2.42 (1)	Mo–C(3)	2.42 (1)
Mo–C(2)	2.35 (1)	Mo–C(5)	2.43 (1)
P(1)–C(1)	1.71 (1)	P(2)–C(3)	1.73 (1)
C(2)–C(1)	1.43 (2)	C(2)–C(3)	1.43 (2)
C(2)–C(4)	1.51 (2)		
P(1)–C(5)	1.73 (1)	P(2)–C(5)	1.73 (1)
P(1)–C(11)	1.85 (1)	P(2)–C(21)	1.821 (9)
P(1)–C(12)	1.804 (8)	P(2)–C(22)	1.789 (9)

Angles

C(1)–Mo–C(10)	164.9 (6)	C(3)–Mo–C(20)	166.1 (5)
C(5)–Mo–C(30)	171.0 (6)		
P(1)–C(1)–C(2)	125 (1)	P(2)–C(3)–C(2)	123 (1)
C(1)–C(2)–C(4)	120 (1)	C(3)–C(2)–C(4)	116 (1)
C(1)–C(2)–C(3)	124 (1)		
C(5)–P(1)–C(1)	102.6 (7)	C(5)–P(2)–C(3)	102.8 (6)
C(5)–P(1)–C(11)	112.2 (7)	C(5)–P(2)–C(21)	112.1 (6)
C(5)–P(1)–C(12)	114.3 (7)	C(5)–P(2)–C(22)	115.0 (6)
P(1)–C(5)–P(2)	114.1 (7)		
C(1)–P(1)–C(11)	109.3 (7)	C(3)–P(2)–C(21)	110.7 (6)
C(1)–P(1)–C(12)	114.5 (6)	C(3)–P(2)–C(22)	113.0 (6)
C(11)–P(1)–C(12)	104.1 (5)	C(21)–P(2)–C(22)	103.4 (5)

$10 \leq \theta \leq 13°$. From systematic absences, the space group was determined as *Pbca*. Intensity data showed only a small decrease of 2% during data collection. For the same reasons as for compound 2, no absorption correction was carried out. The Mo atom was located by the Patterson map (SHELXS-86),[14] the remaining parts of the molecule in a series of least-squares refinements and difference Fourier maps. The atoms of the solvent tetrahydrofuran molecule (one half-molecule in the asymmetric unit—site occupancy 0.5 for the oxygen atom—with two carbon atoms showing a distinct disorder and site occupancy 0.25) were found by an alternating sequency of least-squares refinements and Fourier maps. The four phenyl rings were refined as rigid groups, and all hydrogen atoms were calculated in fixed positions. This resulted in residuals $R = 0.0723$ and $R_w = 0.0562$ and a satisfactory difference Fourier map with residual contours well below 1 e Å^{-3} near the disordered solvent molecule. The atomic positional parameters for the non-hydrogen atoms are listed in Table III. Selected bond distances and angles for 4 and 5 are listed in Tables IV and V, respectively.

Supplementary material for both structures has been deposited.

Acknowledgment. This work has been generously supported by the Deutsche Forschungsgemeinschaft (Leibniz Programm), by the Fonds der Chemischen Industrie, and by HOECHST AG. Mr. J. Riede is thanked for establishing the crystallographic data sets.

Registry No. 1, 132749-41-8; 2, 125995-74-6; 4, 142131-40-6; 4·THF, 142131-41-7; 5, 142159-55-5; 5·$^1/_2$THF, 142159-56-6; (2,5-norbornadiene)molybdenum tetracarbonyl, 12146-37-1; (cycloheptatriene)molybdenum tricarbonyl, 12083-34-0.

Supplementary Material Available: Tables of hydrogen atom positions, bond distances, interbond angles, anisotropic thermal parameters, and root-mean-square amplitudes of anisotropic displacement (20 pages). Ordering information is given on any current masthead page.

OM9201066

Syntheses and Molecular Structures of Hexasilylbenzenes and Disilylacetylenes

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Received November 13, 1991

For the preparation of bis(phenylsilyl)acetylene (2), Li_2C_2 has been obtained from $Br_2CHCHBr_2$ (or ClCHCHCl) and alkyllithium reagents and reacted with $ClSiH_2Ph$. HC_2Na and $BrSiH_2Ph$ afford the primary product HC_2SiH_2Ph (4), from which, via metalation and treatment with H_3SiBr, $H_3SiC_2SiH_2Ph$ (5) can be generated. 2 could not be trimerized when treated with various transition metal catalysts. Hexakis(phenylsilyl)benzene (1) is available from the reaction of $PhSiH_2Cl$ and C_6Br_6 with Mg in tetrahydrofuran, and the *p*-tolyl analogue 3 has been prepared similarly using *p*-$TolSiH_2Cl$. The crystal and molecular structures of 1–3 have been determined by single-crystal X-ray diffraction. 2 has standard disilylalkyne dimensions. In contrast to the hexakis(trimethylsilyl) analogue, 1 and 3 feature planar central benzene rings with the arylsilyl groups at opposite corners above and below the plane. 1 crystallizes from CCl_4 with two independent molecules and three solvent molecules of CCl_4 in the asymmetric unit (rhombohedral, space group $R\bar{3}$). Both 1 and 3 crystallize from ethyl acetate without solvent, but only the structure of 3 has been determined (rhombohedral, space group $R\bar{3}$). 2 crystallizes from the melt (monoclinic, space group $P2_1/a$).

Introduction

Phenylsilane, $H_3SiC_6H_5$ (or silylbenzene), and one of the three possible isomeric disilylbenzenes, *p*-$(H_3Si)_2C_6H_4$, are the only silylbenzenes described in the literature with no further substituents at silicon but hydrogen.[1-3] For the synthetic chemist, the fully substituted derivative hexasilylbenzene (A), the hexasilyl analogue of hexamethylbenzene (B), remains a challenge.

While many of the fully *methylated* silylbenzenes, mostly poly(trimethylsilyl)benzenes, are well represented in the organosilicon literature,[4-6] it was not until the work

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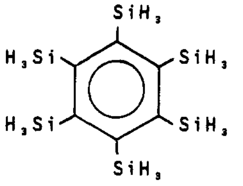
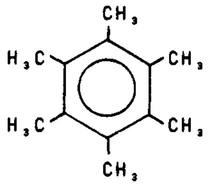


A



B

of Gilman et al.[5] and of Sakurai et al.[6] that hexakis(trimethylsilyl)benzene and its hexakis(dimethylsilyl) and hexakis(bromodimethylsilyl) precursors could finally be described as the first species with a benzene ring bearing six silicon atoms. As might be expected, $C_6(SiMe_3)_6$ was shown to be an extremely crowded molecule, with the bulkiness of the trimethylsilyl groups strongly affecting the molecular structure and the reactivity pattern.[6] Though somewhat reduced, the same effect is also noticeable with the partially trimethylsilylated benzene derivatives.[4]

In order to learn more about the chemistry of persilylated benzene compounds *not* strongly dominated by steric effects, investigations of molecules with as many SiH functions as possible were desirable. Though A is the natural target molecule for such a program, it turns out that this basic member of the series is also the synthetically most difficult one, since standard reactions fail with the components required for the synthesis of this compound.

In a recent study of the chemistry of the polysilyl*methanes*[7] it could be shown, however, that *phenylsilyl* groups $PhSiH_2$ can be used as "masked" silyl groups, since there are efficient methods available to remove the phenyl substituents[8] and replace them by hydrogen. In order to employ the same strategy for polysilylbenzenes, we have therefore undertaken the synthesis of poly(arylsilyl)benzene molecules. We present here some of our initial results, which also include—for obvious reasons—bis(arylsilyl)acetylenes.

Our investigations are part of a current project oriented at the preparation of silicon carbide thin films through direct plasma-enhanced or thermal vapor deposition, or remote plasma decomposition, of precursors with tailor-made stoichiometry, as already practiced with bis-, tris-, and tetrakis(silyl)*methane*.[9-12] Several silylated benzene molecules have previously been considered for such usage in the patent literature, with thermally induced decomposition as the main deposition technique.[13]

Results

Preparation and Properties of the Compounds. Two major pathways have been investigated for the synthesis of hexakis(phenylsilyl)benzene (1). The *first* of these is suggested by the successful preparation of hexamethyl- or hexaethylbenzene by trimerization of but-2-yne or hex-3-yne, respectively.[14] For the analogous cyclization to give $(PhSiH_2)_6C_6$ (1), the precursor bis(phenylsilyl)acetylene (2) was required. This compound is available through the reaction of dilithioacetylene with chlorophenylsilane. C_2Li_2 can be prepared from tetrabromoethane or *trans*-dichloroethylene upon treatment with methyllithium or *n*-butyllithium, respectively, in ether solvent, as described in the literature.[15,16] Improved methods for the preparation of $PhSiH_2Cl$ have been published from this laboratory only recently.[17,18]

$$Br_2CHCHBr_2 + 4MeLi \rightarrow 2CH_4 + 2MeBr + 2LiBr + Li_2C_2 \quad (1)$$

$$HClC{=}CClH + 3n\text{-}BuLi \rightarrow 2n\text{-}C_4H_{10} + n\text{-}BuCl + LiCl + Li_2C_2 \quad (2)$$

$$Li_2C_2 + 2PhSiH_2Cl \rightarrow 2LiCl + \underset{2}{PhH_2SiC{\equiv}CSiH_2Ph} \quad (3)$$

The yields of the reaction according to eq 3 are virtually independent of the method of preparation employed for Li_2C_2 (eqs 1 and 2). The alkyne 2 is isolated as a colorless distillable liquid, only moderately sensitive to air and moisture, which solidifies at 9 °C to give transparent monoclinic crystals. NMR, vibrational, and mass spectrometric data support the composition and structure of 2.

The analogous bis(*p*-tolylsilyl)acetylene, a potential precursor for hexakis(*p*-tolylsilyl)benzene (3), has not been prepared, since cyclization experiments with 2 failed to give 1 (below).

(Phenylsilyl)acetylene ($PhSiH_2C{\equiv}CH$, 4) was obtained as a byproduct in some of the syntheses of 1. Experiments with the stoichiometry adjusted to 1:1 for $NaC{\equiv}CH$ and $PhSiH_2Br$, instead of 1:2 for Li_2C_2 and $PhSiH_2Cl$, afforded a 64% yield of the singly silyl-substituted acetylene:

$$NaC{\equiv}CH + PhSiH_2Br \rightarrow NaBr + \underset{4}{PhSiH_2C{\equiv}CH} \quad (4)$$

The compound is a colorless, distillable liquid, stable in air (bp 51 °C (10 Torr)). Analytical and spectroscopic data are summarized in the Experimental Section.

When a procedure previously employed with trimethylsilylacetylides is followed,[19] compound 4 can be metalated with a reagent RMgX and reacted further with H_3SiBr to give (phenylsilyl)silylacetylene ($PhSiH_2C{\equiv}CSiH_3$, 5). The metalation reaction is accompanied by some SiH and SiC≡ cleavage leading, e.g., with *i*-PrMgCl, to isopropylphenylsilane, (isopropylphenylsilyl)acetylene, and (isopropylphenylsilyl)silylacetylene as byproducts, which are difficult to separate. The compounds were identified mainly through their NMR spectra.

$$PhSiH_2C{\equiv}CH + i\text{-}PrMgCl \rightarrow PhSiH_2C{\equiv}CMgCl + C_3H_8 \quad (5)$$

$$PhSiH_2C{\equiv}CMgCl + H_3SiBr \rightarrow MgBrCl + \underset{5}{PhSiH_2C{\equiv}CSiH_3} \quad (6)$$

$$4 + i\text{-}PrMgCl/BrSiH_3 \rightarrow Ph(i\text{-}Pr)SiH_2,\ Ph(i\text{-}Pr)SiHC{\equiv}CH,\ Ph(i\text{-}Pr)SiHC{\equiv}CSiH_3 \quad (7)$$

All attempts to induce cyclization of the alkyne 2 by action of various metal catalysts, as employed in the trimerization

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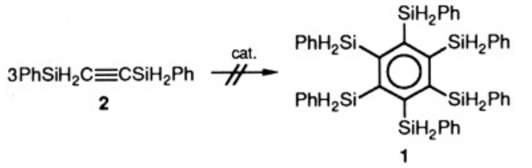
of dialkylacetylenes, or by thermal and photochemical induction have to-date been unsuccessful (eq 8). It should

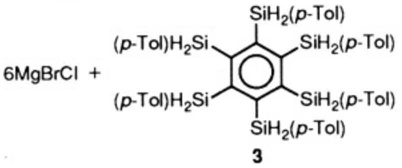


(8)

be noted that this result is perhaps not unexpected, since experiments with disilylacetylene ($H_3SiC{\equiv}CSiH_3$) have also failed.[19] In all cases, only minor amounts of intractable polymeric materials were obtained. It appears that intermolecular hydrosilylation is clearly favored over alkyne trimerization. The *second* method under investigation was the in situ Grignard reaction of hexabromobenzene with chlorophenylsilane and magnesium in boiling tetrahydrofuran. The yield of crude product amounts to ca. 45%, but recrystallized material (from diethyl ether) is finally obtained in much lower (16%) yield. With chloro-*p*-tolylsilane as the reaction component, instead of chlorophenylsilane, the analogous *p*-tolyl compound (*p*-Tol-$SiH_2)_6C_6$ (**3**) is generated in very similar yield (40 and 17%, respectively):

$$6PhSiH_2Cl + C_6Br_6 + 6Mg \longrightarrow 6MgBrCl + \mathbf{1} \quad (9)$$

$$6p\text{-}TolSiH_2Cl + C_6Br_6 + 6Mg \longrightarrow$$



(10)

The two hexakis(arylsilyl)benzenes **1** and **3** form colorless crystals at room temperature, with melting points of 172 and 202 °C, respectively. They are stable in air at room temperature, sparingly soluble in most of the common solvents, and only very slowly attacked by water, acid, or base. In fact, is has been noted that both compounds crystallize with hydrate water from wet solvents, which is difficult to remove, but does not cause hydrolysis. The NMR data feature a large low-field shift of the ^{13}C signals of the central benzene carbon atoms (151.0 and 151.1 ppm for **1** and **3**, respectively). This result is in agreement with the values given for hexakis(trimethylsilyl)benzene by Sakurai et al. (162.3 and 148.9 ppm). ^1H and ^{29}Si resonances of the SiH_2 groups are very similar for **1** and **3**, and the absolute values for δ and $J(SiH)$ are close to those of simple arylsilane reference compounds. There is no evidence for inequivalence of the silyl substituents in solution (chloromethane solvents). In the mass spectra (electron impact, 70 eV), the molecular ions are observed as parent peaks, with the loss of a phenyl group (*p*-tolyl group) as the dominating fragmentation. IR absorptions (KBr pellet) are indicative of the sole presence of SiH_2 groups in the two compounds, as shown by bands at 2158 (2154) and 2148 (2138) cm^{-1} for ν(as) and ν(s), respectively, in **1** (**3**).

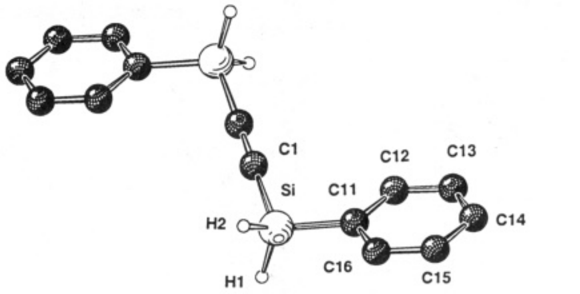


Figure 1. Molecular structure of bis(phenylsilyl)ethyne (**2**) (SCHAKAL). (The compound has a center of inversion.)

Crystal and Molecular Structures. The acetylene **2** crystallized from the melt upon slow cooling of the liquid compound in the absence of a solvent, and small triclinic single crystals could be cut from a crop of large specimens. Hexakis(phenylsilyl)benzene (**1**) was found to crystallize with carbon tetrachloride molecules from this solvent (**1a**). Some of these crystal solvent molecules are disordered, rendering the solution of the structure of **1a** somewhat unsatisfactory. Triclinic crystals were obtained from ethyl acetate that contained no molecules of solvent in the lattice (**1b**). The structure of this phase was not solved for economic reasons, because of the extremely large data set to be expected for the unit cell. The tolyl analogue **3** also crystallized from ethyl acetate as rhombohedral crystals, which did not contain solvent.

Crystal data of the compounds are summarized in Table I.

The lattice of **bis(phenylsilyl)acetylene (2)**, space group $P2_1/a$, is found to contain crystallographically centrosymmetrical molecules, with the center of inversion in the middle of the C≡C triple bond (Figure 1). These molecules are stacked into columns with the linear SiC≡CSi units parallel. The phenyl rings of neighboring molecules also have parallel orientation.

The details of the molecular dimensions are not unusual as far as the Si–C and C–C bond lengths and the bond angles are concerned (Table II), meaning that there is no evidence for a special silicon substituent effect on the alkyne group as compared to the situation in alkylalkynes. Tetrakis[(trimethylsilyl)ethynyl]silane and related compounds can serve as reference materials in this context.[19] The silane hydrogen atoms could be located unambiguously, and their positions indicate only minor distortions of the tetrahedral geometry about the silicon atoms. The phenyl rings show alternations in the C–C bond distances and C–C–C bond angles, in line with predictions for aryl groups bearing electropositive substituents.[20]

We conclude from the structural data that the low reactivity of the compound, e.g., in cyclization reactions (eq 8), is not a consequence of major changes in the C≡C bonding characteristics induced by two silicon substituents, but rather an effect based on the low polarity and strong shielding by the "silabenzyl" groups.

The molecules of **hexakis(*p*-tolylsilyl)benzene (3)** are stacked in parallel columns in the rhombohedral cell, with a 3-fold axis passing through the centers of the benzene rings (Figure 2). The benzene center is also a center of inversion relating the silabenzyl groups at opposite corners above and below the benzene plane. The point group of the individual molecule is thus S_6.

The silicon–carbon distance to the central ring is a little larger than the distance to the *p*-tolyl group, perhaps reflecting some crowding at the central ring and the combined inductive effects of six electropositive silicon substituents at this ring (Table III). In agreement with this assumption, the *p*-tolyl C–C distances are normal (average 1.387 Å), with very little variations, while the C–C distances of the central ring are very significantly longer [1.416(1) Å]. Though not required by symmetry, the ring angles of the benzene ring are exactly 120.0°, and the ring is strictly planar. As expected, the *p*-tolyl rings are somewhat distorted, but within the usual limits. The hydrogen atoms

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Table I. Crystal Data and Structure Determination

	1·1.5CCl$_4$	2	3
formula	$C_{42}H_{42}Si_6 \cdot 1.5CCl_4$	$C_{14}H_{14}Si_2$	$C_{48}H_{54}Si_6$
mol mass	715.307	238.440	799.480
cryst dimens (mm)	0.1 × 0.3 × 0.5	0.3 × 0.35 × 0.35	0.30 × 0.25 × 0.45
temp (°C)	−50	−50	−23
cryst syst	rhombohedral	monoclinic	rhombohedral
space group	$R\bar{3}$ (No. 148)	$P2_1/a$ (No. 14)	$R\bar{3}$ (No. 148)
a (Å)	18.089 (2)	15.709 (2)	22.407 (3)
b (Å)	18.089 (2)	5.766 (1)	22.407 (3)
c (Å)	48.428 (7)	7.676 (1)	8.132 (2)
α (deg)	90	90	90
β (deg)	90	95.93 (1)	90
γ (deg)	120	90	120
V (Å^3)	8385.4	692.8	3535.9
ρ_{calcd} (g cm^{-3})	1.124	1.143	1.126
Z	6	2	3
$F(000)$	3660	252	1278
μ(Mo Kα) (cm^{-1})	4.6	2.22	2.0
radiatn (λ = 0.71069 Å, graphite monochromator)	Mo Kα	Mo Kα	Mo Kα
diffractometer	Syntex P2$_1$		CAD4
scan	ω	ω	ω
scan range (θ) (deg)	2–23	2–25	2–27
hkl range	5,+15,+53	±18,+6,+9	±28,+28,+10
no. of measd reflcns	2973	1453	3621
no. of unique reflcns	2598	1216	1712
R_{int}	0.031	0.028	0.013
no. of obsd reflcns	1713	1004	1564
F_o	$\geq 4\sigma(F_o)$	$\geq 4\sigma(F_o)$	$\geq 2\sigma(F_o)$
refined params	201	101	106
weighting scheme	$w = 1/(\sigma(F_o) + kF_o^2)$		
weighting param ($1/k$)	3.0357/0.000053	2.5326/0.0	1.5897/0.00183
H atoms (found/calcd)	4/10	14/–	9/–
R	0.060	0.036	0.043
R_w	0.052	0.039	0.068
(shift/error)$_{max}$	0.001	0.001	0.001
$\Delta\rho_{fin}$(max/min) (e Å^{-3})	+0.63/−0.58	+0.21/−0.22	+0.51/0.46

Table II. Selected Bond Distances (Å) and Angles (deg) of Compound 2[a]

Si–C(11)	1.856 (2)	C(13)–C(14)	1.374 (3)
Si–C(1)	1.831 (2)	C(14)–C(15)	1.371 (3)
C(1)–C(1)′	1.196 (4)	C(15)–C(16)	1.385 (3)
C(11)–C(12)	1.398 (3)	Si–H(1)	1.40 (2)
C(11)–C(16)	1.390 (3)	Si–H(2)	1.45 (3)
C(12)–C(13)	1.379 (3)		
C(11)–Si–C(1)	110.6 (1)	C(1)–Si–H(1)	105.9 (8)
Si–C(1)–C(1)′	179.8 (2)	C(11)–Si–H(2)	110.5 (8)
Si–C(11)–C(12)	122.9 (1)	C(1)–Si–H(2)	107.1 (8)
C(11)–Si–H(1)	111.9 (8)	H(1)–Si–H(2)	111 (1)

[a] Standard deviations in parentheses; see Figure 1 for atomic numbering.

Table III. Selected Bond Distances (Å) and Angles (deg) of Compound 3[a]

Si–C	1.893 (2)	C(4)–C(5)	1.389 (3)
Si–C(1)	1.862 (2)	C(5)–C(6)	1.384 (3)
C(1)–C(2)	1.392 (2)	C–C′	1.416 (1)
C(1)–C(6)	1.393 (3)	Si–H(1)	1.42 (2)
C(2)–C(3)	1.388 (3)	Si–H(2)	1.32 (2)
C(3)–C(4)	1.380 (3)		
C–Si–C(1)	114.3 (1)	C–Si–H(2)	106.6 (8)
C–C′–Si	120.0 (1)	C(1)–Si–H(1)	113.5 (8)
C–C′–C″	120.0 (2)	C(1)–Si–H(2)	112.4 (8)
C–Si–H(1)	107.6 (9)	H(1)–Si–H(2)	101 (1)

[a] Standard deviations in parentheses; see Figure 2 for atomic numbering.

at silicon have been located, and the geometry observed for the silicon environment is close to tetrahedral, albeit with some widening of the C–Si–C angle to 114.3 (1)°.

The crystals containing **hexakis(phenylsilyl)benzene** and carbon tetrachloride, **1a**, are also rhombohedral, and the individual molecules **1** (point group S_6) are also stacked in columns (Figure 3), with molecular dimensions almost identical with those of **3** (Table IV). Owing to the solvent disorder, the accuracy of the data is generally less great, and therefore, a discussion of small details would not be meaningful. Although no major structural changes are expected from the introduction of the methyl groups in the para positions of the phenyl rings (**1**–**3**), the close relation of the two structures is proof that the features discussed for **3** [planarity, elongated C–C(ring) distances, S_6 symmetry, etc.] are quite general for hexasilylbenzenes

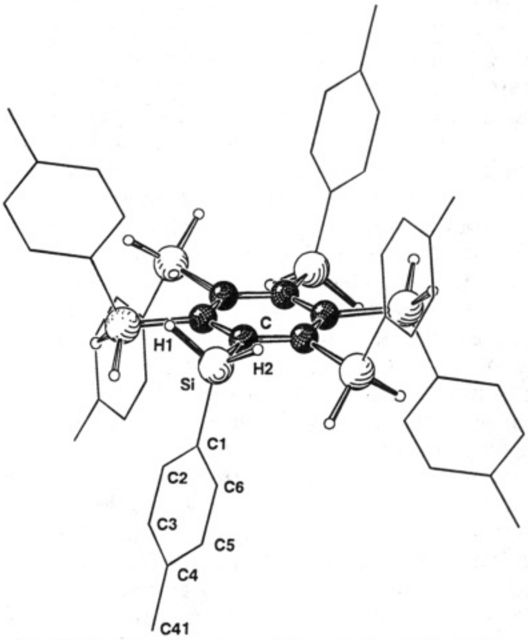

Figure 2. Molecular structure of hexakis(p-tolylsilyl)benzene (**3**) (SCHAKAL). (The compound has a 3-fold inversion axis.)

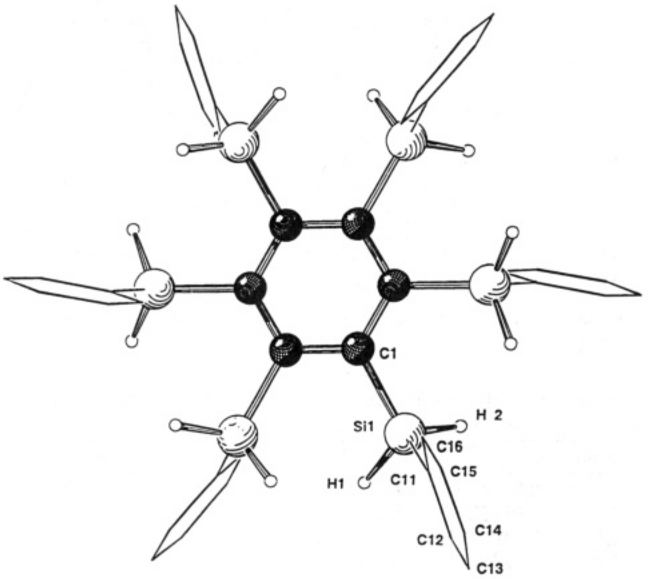

Figure 3. Molecular structure of hexakis(phenylsilyl)benzene 1 in **1a** ($1\cdot1.5CCl_4$; SCHAKAL). (The molecule has a 3-fold inversion axis. Only one of two independent molecules in the unit cell is shown.)

Table IV. Selected Bond Distances (Å) and Angles (deg) of Compound 1a[a]

Si(1)–C(1)	1.892 (5)	C(1)–Si(1)–C(11)	114.1 (2)
Si(1)–C(11)	1.862 (6)	C(1)′–C(1)–Si(1)	120.0 (6)
C(11)–C(12)	1.378 (8)	C(1)′–C(1)–C(1)″	120.0 (8)
C(12)–C(13)	1.373 (8)	C(1)–Si(1)–H(1)	110.3
C(13)–C(14)	1.376 (9)	C(1)–Si(1)–H(2)	106.3
C(14)–C(15)	1.36 (1)	C(11)–Si(1)–H(1)	108.3
C(15)–C(16)	1.399 (8)	C(11)–Si(1)–H(2)	113.2
C(11)–C(16)	1.391 (7)	H(1)–Si(1)–H(2)	104.2
C(1)–C(1)′	1.416 (4)		
Si(1)–H(1)	1.516		
Si(1)–H(2)	1.346		
Si(2)–C(2)	1.898 (5)	C(2)–Si(2)–C(21)	117.9 (3)
Si(2)–C(21)	1.864 (6)	C(2)′–C(2)–Si(2)	120.1 (7)
C(21)–C(22)	1.399 (7)	C(2)′–C(2)–C(2)″	120.0 (9)
C(22)–C(23)	1.387 (8)	C(2)–Si(2)–H(3)	109.9
C(23)–C(24)	1.365 (9)	C(2)–Si(2)–H(4)	102.4
C(24)–C(25)	1.357 (9)	C(21)–Si(2)–H(3)	109.0
C(25)–C(26)	1.394 (8)	C(21)–Si(2)–H(4)	113.0
C(21)–C(26)	1.387 (8)	H(3)–Si(2)–H(4)	103.6
C(2)–C(2)′	1.414 (5)		
Si(2)–H(3)	1.374		
Si(2)–H(4)	1.409		

[a] Standard deviations in parentheses; see Figure 3 for atomic numbering. There are two crystallographically independent molecules in the unit cell, with silicon atoms Si(1) and Si(2), respectively.

with less severe steric hindrance, as, for example, compared with hexakis(trimethylsilyl)benzene.[6] The crystals of **1a** contain two independent molecules (A, B) in the asymmetric unit, but these differ only very little in their geometry. The silicon atoms deviate from the best plane through the central benzene ring by 0.153 Å for molecule A and by 0.185 Å for molecule B. For **3** this deviation is 0.117 Å.

Preparative and structural studies on other polysilylbenzenes, including A, and work on the deposition of silicon carbide films with these molecules as feedstock materials are in progress.

Experimental Section

All experiments were carried out under pure, dry nitrogen. Solvents were purified, dried, and stored over molecular sieves in a nitrogen atmosphere. NMR: $CDCl_3$, C_6D_6 as solvent, tetramethylsilane as internal standard, JEOL JNM-PMX 60, Bruker WP 100 SY, JEOL GX 270, JEOL GX 400 spectrometers. IR: moulded KBr grindings or films between KBr plates, Nicolet FT 5 DX spectrometer. Mass spectra: electron impact source (70 eV), Varian MAT 90 spectrometer.

Starting Materials. Phenylsilane was obtained by $LiAlH_4$ reduction of phenyltrichlorosilane.[10] Chlorophenylsilane and bromophenylsilane were prepared via halogenation of phenylsilane with the corresponding hydrogen halides.[9–11]

Dilithioacetylide was prepared from 1,1,2,2-tetrabromoethane or *trans*-1,2-dichloroethene and alkyllithium compounds, according to published procedures.[15,16] All other chemicals were commercially available.

Phenylsilylethyne (4). A 54.3-g sample of a 18% sodium acetylide suspension in xylene/petroleum ether (0.204 mol) was filtered through a glass filter funnel (G4) and the solid residue washed twice with 5 mL of diethyl ether. The acetylide was suspended in 100 mL of THF, and at 0 °C, a solution of 40.61 g (0.217 mol) of bromophenylsilane in 150 mL of ether was added. The suspension was allowed to warm to room temperature within 3 h and then stirred for an additional 16 h at this temperature. After completion of the reaction by refluxing for 3 h, the whole mixture was poured on crushed ice. The layers were separated and the water phase was washed twice with 100 mL of hexane. The unified organic layers were dried with magnesium sulfate. Phenylsilylethyne was isolated by distillation as a colorless liquid boiling at 51 °C (10 Torr). ^1H NMR (C_6D_6): δ 4.62 (d, SiH_2, J(HSiCCH) = 1.22 Hz), 2.10 (t, $\equiv$CH, J(HSiCCH) = 1.22 Hz), 7.12 (m, 3 H), 7.51 (m, 2 H). ^{13}C NMR (C_6D_6): δ 98.47 (dt, $\equiv$CH, J(CH) = 240 Hz, J(CCSiH) = 3.68 Hz), 81.22 (dt, $SiH_2C\equiv$, J(CCH) = 43.2 Hz, $2J$(CSiH) = 6.44 Hz), 128.37 (m, C1), 128.46 (dm, C3,5, J(CH) = 159 Hz), 130.5 (dtm, C4, J(CH) = 160 Hz, J(CCCH) = 7.4 Hz), 135.4 (dm C2,6, J(CH) 159 Hz); $\{^1H\}$: J(CSi) = 90.1 Hz, J(CCSi) = 16.0 Hz. ^{29}Si NMR (C_6D_6): δ –60.17 (tq, SiH_2, J(SiH) = 216.0 Hz, J(SiCCH) = 5.5 Hz). MS (m/z) (rel intensity): 131 [C_8H_8Si] 100, 105 [C_6H_5Si], 77 [C_6H_5]. IR (cm^{-1}): 3282 (s, $\nu(\equiv C—H)$), 3072–2870 (m, ν(Ar—H)), 2164 (vs, $\nu(SiH_2)$), 2041 (s, $\nu(C\equiv C)$), 1959—1773 (w, comb(Ar—R)), 1591, 1486 (m, $\nu(C\equiv C)_{Ar}$), 1430, 1119 (s, comb(Ar—Si)), 941 (vs, $\delta(SiH_2)$), 845 (vs, $\gamma(SiH_2)$), 695 (vs, $\tau(SiH_2)$), 632 (s), 602 (s).

Metalation of 4 and Reaction with Bromosilane. In the course of 100 min a solution of 75.68 g (0.57 mol) of phenylsilylethyne in 150 mL of ether and 285 mL (0.57 mol) of a 2 M solution of isopropylmagnesium chloride in ether were simultaneously added to 150 mL of ether. With evolution of propane, a white precipitate formed immediately. After the addition was completed, the reaction mixture was cooled to –78 °C and 63 g (0.57 mol) of bromosilane was added over a period of 45 min. The reaction was allowed to proceed at this temperature for 1 h and stirred at room temperature for additional 3 h. Volatile components were removed in a vacuum and precipitated salts filtered off. Vacuum distillation gave four fractions. Isopropylphenylsilane, (phenylsilyl)silylethyne and (isopropylphenylsilyl)silylethyne were identified in these fractions: fraction I [5.01 g, bp 35 °C (0.7 Torr)] predominantly isopropylphenylsilane; fraction II [1.14 g, bp 45 °C (0.7 Torr)] predominantly (phenylsilyl)silylethyne; fraction III [5.63 g, 54 °C (0.7 Torr)] predominantly (isopropylphenylsilyl)silylethyne; fraction IV [12.3 g, 62 °C (0.5 Torr)] pure (isopropylphenylsilyl)silylethyne.

Isopropylphenylsilane. ^1H NMR (C_6D_6): δ 4.32 (d, SiH_2, 2 H, J = 2.44 Hz), 1.02 (m, 7 H, i-Prop), 7.16 (m, 3 H), 7.46 (m, 2 H). ^{13}C NMR (C_6D_6): δ 11.14 (CH, J(SiC) = 55.15 Hz), 19.10 (CH_3), 128.22 (C3,5), 129.78 (C4), 135.85 (C2,6). ^{29}Si NMR ($CDCl_3$): δ –20.71 (tm, SiH_2, J(SiH) = 195.6 Hz). MS (m/z) (rel intensity): 150 [$C_9H_{14}Si$], 121 [C_9H_{13}], 107 [C_6H_7Si] 100.

(Phenylsilyl)silylethyne. ^1H NMR (C_6D_6): δ 4.60 (s, SiH_2), 3.74 (s, SiH_3), 7.18 (m, 3 H), 7.50 (m, 2 H). ^{13}C NMR (C_6D_6): δ 106.43 (C^α, J(SiC) = 85.48 Hz, J(SiCC) = 13.79 Hz), 110.36 (C^β, J(SiC) = 84.56 Hz, J(SiCC) = 10.01 Hz), 128.45 (C3,5), 130.49 (C4), 135.43 (C2,6). ^{29}Si NMR ($CDCl_3$): δ –88.39 (q, SiH_3, J(SiH) = 219.1 Hz), –61.01 (t(t), SiH_2, J(SiH) = 215.95 Hz). MS (m/z) (rel intensity): 161 [$C_8H_{10}Si_2$], 147 [131 + 16{O}], 131 [C_8H_7Si] 100, 105 [C_6H_5Si].

(Isopropylphenylsilyl)silylethyne. ^1H NMR (C_6D_6): δ 4.54 (s, SiH), 3.82 (s, SiH_3), 1.05 (m, 7 H, i-Prop), 7.20 (m, 3 H), 7.56 (m, 2 H). ^{13}C NMR (C_6D_6): δ 113.26 (m, $\equiv CSiH_3$), 105.19 (m, PhSiHC$\equiv$), 17.8, 17.6 (qm, CH_3, J(CH) = 124 Hz, diastereotopic methyl groups), 12.8 (dm, CH, *J*(CH) = 123 Hz), 128.4 (dm, C3,5, *J*(CH) = 159 Hz), 130.3 (dtm, C4, *J*(CH) = 159 Hz, *J*(CCCH) = 7.9 Hz), 135.2 (dm, C2,6, *J*(CH) = 158 Hz); {^{1}H}: C$^\alpha$, *J*(CSi) = 85.6 Hz, *J*(CCSi) = 11.7 Hz, C$^\beta$, *J*(CSi) = 78.7 Hz, *J*(CCSi) = 13.5 Hz. ^{29}Si NMR (C_6D_6): δ −28.55 (dm, SiH, *J*(SiH) = 207.3 Hz), −88.13 (q, SiH_3, *J*(SiH) = 218.12 Hz). MS (*m*/*z*) (rel intensity): 204 [$C_{11}H_136Si_2$], 173 [$C_{11}H_{13}Si$], 161 [$C_8H_9Si_2$] 100, 131 [C_8H_7Si], 105 [C_6H_5Si]. IR (cm^{-1}): 3070–2864 (s, ν(Ar—H) + ν(Alk—H)), 2178, 2142 (vs, ν(Si—H)), 2039 (w, ν(C≡C)), 1957–1767 (w, comb(Ar-R)), 1587, 1487 (m, $\nu(C{\equiv}C)_{Ar}$), 1460 (s, $\delta_{asym}(CH_3)$), 1428, 1112 (s, comb(Ar—Si)), 1387, 1365 (m, $\delta_{sym}(CH_3)$), 1006 (s), 922 (vs), 879 (s), 795 (vs), 731 (s), 700 (s), 679 (s), 647 (m), 621 (w).

Bis(phenylsilyl)ethyne (2). A solution of 40.4 g (0.147 mol) of *trans*-dichloroethene in 250 mL of ether was added to a mixture of 500 mL of 2.5 M *n*-butyllithium in hexane and 400 mL of ether over a period of 3 h at 0 °C. The cloudy suspension was slowly warmed to room temperature and stirred for an additional 20 h. After cooling to −78 °C, 144 g (1.001 mol) of chlorophenylsilane in 500 mL of diethyl ether was added in the course of 4 h. Subsequently, the mixture was warmed to room temperature, stirred for 16 h, and refluxed for additional 3 h. The solvents were removed under reduced pressure and the salts precipitated with 500 mL of pentane and filtered off. Vacuum distillation gave 67.74 g (0.284 mol, 68%) of bis(phenylsilyl)ethyne. A similar experiment with the dilithioacetylide prepared from 3.64 g (0.01 mol) of 1,1,2,2-tetrabromoethane and 0.04 mol of methyllithium and further reaction with 2.85 g (0.02 mol) of chlorophenylsilane gave 1.74 g (73%) of bis(phenylsilyl)ethyne. Bp: 124 °C (0.7 Torr). Mp: 9 °C. ^{1}H NMR ($CDCl_3$): δ 4.67 (s, SiH_2), 7.36 (m, 3 H), 7.68 (m, 2 H). ^{13}C NMR (C_6D_6): δ 110.34 (m, C≡C), 128.2 (m, C1), 128.5 (dm, C3,5, *J*(CH) = 160 Hz), 130.6 (dtm, C4, *J*(CH) = 159 Hz, *J*(CCCH) = 7.4 Hz), 135.5 (dm, C2,6, *J*(CH) = 160 Hz); {^{1}H}: 109.69 (C≡C, *J*(CSi) = 84.0, *J*(CCSi) = 13.6 Hz); 127.78 (C1); 128.13 (C3,5); 130.23 (C4); 135.03 (C2,6). ^{29}Si NMR ($CDCl_3$): δ −60.86 (tt, SiH_2, *J*(SiH) = 216.9 Hz, *J*(SiCCH) = 6.4 Hz). MS (*m*/*z*) (rel intensity): 238 [$C_{14}H_{14}Si_2$], 207 [$C_{14}H_{11}Si$] 100, 183 [$C_{12}H_{11}Si$], 160 [$C_8H_8Si_2$], 131 [C_8H_7Si], 105 [C_6H_5Si]. IR (cm^{-1}): 3072–2853 (s, ν(Ar—H)), 2162 (vs, ν(Si—H)), 1954–1770 (w, comb(Ar–R)), 1589, 1488 (m, $\nu(C{=}C)_{Ar}$), 1432, 1117 (s, comb(Ar—Si)), 940 (s, $\delta(SiH_2)$), 857 (s, $\gamma(SiH_2)$), 694 (s, $\gamma(SiH_2)$), 886 (s), 792 (s), 598 (s). Anal. Calcd for $C_8H_{14}Si_2$: C, 70.52; H, 5.92; Si, 23.56. Found: C, 70.96; H, 5.7; Si, 23.34.

Hexakis(phenylsilyl)benzene (1). A suspension of 24.31 g (0.044 mol) of hexabromobenzene in 440 mL of THF was added in small portions to a mixture of 100 g (1.43 mol) of chlorophenylsilane and 17 g (0.7 mol) of magnesium in 280 mL of boiling THF at such a rate that the solvent remained boiling at reduced external heating. After complete addition and further refluxing for 13.5 h, the mixture was poured onto crushed ice and neutralized with sodium bicarbonate. Hexane (500 mL) was added, and the organic layer was separated. The water phase was extracted twice with 750 mL of hexane; the organic layers were combined and dried with magnesium sulfate. On removal of the solvents, a partially crystalline, yellow solid remained. Repeated recrystallization from ether gave 5.02 g (16%) of pure **1**. Mp: 172 °C. ^{1}H NMR ($CDCl_3$): δ 5.1 (s, SiH_2). ^{13}C NMR ($CDCl_3$): δ 151.03 (cent. benzene). ^{29}Si NMR ($CDCl_3$): δ −39.95 (tt, *J*(SiH) = 199.93 Hz, *J*(SiCCH) = 5.5 Hz). MS (*m*/*z*): 714 [$C_{42}H_{42}Si_6$], 637 [$C_{42}H_{42}Si_6 - C_6H_5$]. IR (cm^{-1}): 2158, 2148 (s, $\nu(SiH_2)$). Anal. Calcd for $C_{42}H_{42}Si_6$: C, 70.52; H, 5.92; Si, 23.56. Found: C, 68.84; H, 6.23; Si, 23.55.

Hexakis(*p*-tolylsilyl)benzene (3). A suspension of 24.55 g (0.045 mol) of hexabromobenzene in 500 mL of THF was added in small portions to a mixture of 80 g (0.51 mol) of chloro-*p*-tolylsilane and 13.2 g (0.54 mol) of magnesium in 400 mL of boiling THF at such a rate that the solvent remained boiling at reduced external heating. After complete addition and further refluxing for 24 h, the mixture was poured onto crushed ice and neutralized with sodium bicarbonate. Trichloromethane (250 mL) was added, and the organic layer was separated. The water phase was extracted with 150 mL of trichloromethane; the organic layers were combined and dried with magnesium sulfate. After removal of the solvent, there remained 15.7 g (45%) of a partially crystalline, yellow solid and a yellow oil. Repeated crystallization from ether/THF gave 6.0 g (17.2%) of pure **3**. Mp: 202 °C. ^{1}H NMR ($CDCl_3$): δ 5.1 (s, SiH_2). ^{13}C NMR ($CDCl_3$): δ 151.10 (cent. benzene). ^{29}Si NMR ($CDCl_3$): δ −40.02 (tt, *J*(SiH) = 198.55 Hz, *J*(SiCCH) = 5.5 Hz). MS (*m*/*z*): 798 [$C_{48}H_{54}Si_6$], 707 [$C_{48}H_{54}Si_6 - C_7H_7$]. IR (cm^{-1}): 2154, 2138 (s, $\nu(SiH_2)$). Anal. Calcd for $C_{48}H_{54}Si_6$: C, 69.35; H, 7.48; Si, 23.17. Found: C, 70.26; H, 7.00; Si, 23.03.

Table V. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 2[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq), Å^2
Si	0.08583 (3)	0.1823 (1)	0.74375 (8)	0.052
C(11)	0.1988 (1)	0.0851 (4)	0.7530 (2)	0.039
C(12)	0.2230 (1)	−0.1237 (4)	0.6796 (3)	0.047
C(13)	0.3077 (1)	−0.1904 (4)	0.6919 (3)	0.052
C(14)	0.3699 (1)	−0.0522 (4)	0.7776 (3)	0.054
C(15)	0.3476 (1)	0.1535 (4)	0.8504 (3)	0.052
C(16)	0.2628 (1)	0.2226 (4)	0.8387 (3)	0.047
C(1)	0.0211 (1)	0.0452 (4)	0.5599 (3)	0.052

[a] *U*(eq) = $(U1U2U3)^1/_3$; *U*1, *U*2, *U*3 are eigenvalues of the *U*(*ij*) matrix.

Table VI. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 3[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq), Å^2
Si	0.03448 (2)	0.16170 (2)	0.01444 (5)	0.027
C	0.01472 (7)	0.06925 (7)	0.0004 (2)	0.023
C(1)	0.04554 (8)	0.20472 (8)	−0.1881 (2)	0.030
C(2)	0.0778 (1)	0.27622 (9)	−0.1975 (2)	0.037
C(3)	0.0866 (1)	0.3098 (1)	−0.3467 (3)	0.039
C(4)	0.0632 (1)	0.2733 (1)	−0.4917 (2)	0.037
C(5)	0.0308 (1)	0.2019 (1)	−0.4832 (2)	0.044
C(6)	0.0211 (1)	0.1682 (1)	−0.3349 (3)	0.040
C(41)	0.0722 (2)	0.3103 (1)	−0.6525 (3)	0.051

[a] *U*(eq) = $(U1U2U3)^1/_3$; *U*1, *U*2, *U*3 are eigenvalues of the *U*(*ij*) matrix.

Table VII. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 1 • 1.5CCl$_4$[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq), Å^2
Si(1)	−0.0043 (1)	0.2313 (1)	0.00316 (3)	0.025
C(1)	−0.0018 (5)	0.0992 (4)	0.0001 (1)	0.017
C(11)	−0.0081 (4)	0.2924 (5)	−0.0306 (1)	0.024
C(12)	0.0118 (5)	0.3982 (5)	−0.0313 (1)	0.038
C(13)	0.0109 (6)	0.4472 (5)	−0.0557 (2)	0.045
C(14)	−0.0101 (6)	0.3909 (7)	−0.0802 (2)	0.046
C(15)	−0.0293 (5)	0.2866 (7)	−0.0804 (1)	0.046
C(16)	−0.0275 (5)	0.2370 (5)	−0.0556 (1)	0.036
Si(2)	0.1026 (1)	0.6722 (1)	0.16284 (3)	0.029
C(2)	0.2347 (4)	0.6694 (6)	0.1667 (1)	0.023
C(21)	0.0358 (4)	0.6841 (4)	0.1948 (1)	0.027
C(22)	0.0465 (5)	0.6463 (5)	0.2207 (1)	0.033
C(23)	−0.0100 (5)	0.6529 (5)	0.2433 (1)	0.040
C(24)	−0.0766 (5)	0.6966 (6)	0.2407 (1)	0.042
C(25)	−0.0869 (6)	0.7348 (6)	0.2159 (2)	0.048
C(26)	−0.0314 (5)	0.7291 (6)	0.1927 (1)	0.046
C(111)	0.33330	0.66670	0.0609 (2)	0.045
Cl(11)	0.2454 (2)	0.5340 (1)	0.04895 (4)	0.058
Cl(12)	0.3330	0.66670	0.09717 (6)	0.067
C(222)	0.66670	0.33330	0.0373 (2)	0.047
Cl(21)	0.5372 (1)	0.2350 (2)	0.02529 (4)	0.061
Cl(22)	0.66670	0.33330	0.07330 (7)	0.080

[a] *U*(eq) = $(U1U2U3)^1/_3$; *U*1, *U*2, *U*3 are eigenvalues of the *U*(*ij*) matrix.

X-ray Structural Analyses of Compounds 1a (1·1.5CCl$_4$), 2, and 3. Single crystals of the compounds were mounted in glass capillaries and examined on a Syntex P2$_1$ (**1a** and **2** at −50 °C) and an Enraf Nonius CAD4 diffractometer (**3**). Crystal data and data collection and refinement information are given in Table I. The lattice parameters were refined from 15 (Syntex) and 25 (CAD4) reflections ($13 < \theta < 16°$). The structures were solved by direct methods. The positions of all non-hydrogen atoms were obtained from the Fourier and difference-Fourier maps and were refined anisotropically. For compounds **2** and **3** all hydrogen atoms were located, for compound **1a** only the hydrogen atoms attached to silicon were located. All hydrogen atoms of **1a** and the (C)H hydrogen atoms of **2** and **3** were included as fixed atoms with $U_{iso(fix)} = 0.05$. The remaining hydrogen atoms were refined isotropically. No absorption corrections were carried out. One of the CCl_4 molecules in **1a** was strongly disordered. Coordinates and equivalent isotropic thermal parameters are shown in Tables V–VII. Crystals of **1** obtained from ethyl acetate were found to crystallize in the triclinic space group $P\bar{1}$ with cell constants $a = 12.411$ (6), $b = 14.863$ (4), $c = 33.298$ (9) Å; $\alpha = 94.87$ (2)°; $\beta = 97.87$ (3)°; $\gamma = 103.99$ (3)°, and probably six molecules in the cell. Programs used for calculations were SHELX 76, SHELXS 88, and PLATON-90.[21]

Acknowledgment. This work has been supported by Deutsche Forschungsgemeinschaft (Leibniz-Programm), by Fonds der Chemischen Industrie, by Bundesministerium für Forschung und Technologie, and—through the donation of chemicals—by Wacker-Chemie GmbH. Mr. J. Riede is thanked for establishing the crystallographic data sets.

Supplementary Material Available: Tables of atomic coordinates and anisotropic temperature factors for **1**–**3** (7 pages). Ordering information is given on any current masthead page.

OM9107000

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(21) Spek, A. L. *Acta Crystallogr. A* 1990, *46*, C31–37.

Preparation of Doubly Acetylide-Bridged Binuclear Platinum–Platinum and Platinum–Palladium Complexes. Structures of $[\{(dppe)Pt(C{\equiv}CPh)_2\}Pt(C_6F_5)_2]$ and $(PMePh_3)_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]$

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Received January 3, 1992

The reaction between [*cis*-$Pt(C{\equiv}CR)_2L_2$] (R = Ph, ^{t}Bu; L_2 = 2 PPh_3, dppe, COD) and [*cis*-$M(C_6F_5)_2(THF)_2$] (M = Pd, Pt; THF = tetrahydrofuran) in a 1:1 molar ratio affords neutral binuclear derivatives of the type $[\{L_2Pt(C{\equiv}CR)_2\}M(C_6F_5)_2]$ in which the $RC{\equiv}C{-}Pt{-}C{\equiv}CR$ group is acting as a bidentate ligand to "$M(C_6F_5)_2$". In contrast, [*cis*-$M(C_6F_5)_2(THF)_2$] reacts with Q_2[*cis*-$Pt(C_6F_5)_2(C{\equiv}CR)_2$] and $Q_2[Pt(C_6F_5)(C{\equiv}CR)_3]$ (R = Ph, Q = $PMePh_3$; R = ^{t}Bu, Q = NBu_4) to give anionic diplatinum and platinum–palladium complexes of types $Q_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR)_2M(C_6F_5)_2]$ and $Q_2[(C_6F_5)(C{\equiv}CR)Pt(\mu\text{-}C{\equiv}CR)_2Pt(C_6F_5)_2]$, respectively. The crystal structures of the complexes $[\{(dppe)Pt(C{\equiv}CPh)_2\}Pt(C_6F_5)_2]$ (**3**) and $(PMePh_3)_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CPh)_2Pt(C_6F_5)_2]$ (**9**) have been established by X-ray diffraction methods. **3** is a binuclear complex in which the unit "(dppe)Pt(σ-$C{\equiv}CPh)_2$" acts as a chelate metallo ligand to "$Pt(C_6F_5)_2$". In contrast, the crystal structure for **9** shows that two identical $[(C_6F_5)_2Pt{-}C{\equiv}CPh]$ units are joined together through η^2 bonding of $C{\equiv}CPh$ groups. This indicates that the complex is formed from the bis(σ-alkynyl)bis(pentafluorophenyl)platinate and the synthon $Pt(C_6F_5)_2$ via migration of one σ-alkynyl group between the two platinum metal centers.

Introduction

Over the past decade there has been growing interest in homo- and heterobinuclear complexes stabilized through bridging acetylide ligands. Much of the interest in those organometallic systems stems from the special bonding situations of $C{\equiv}CR$ groups.[1] In binuclear complexes the $C{\equiv}CR$ ligand appears as a bridging group that exhibits a varying degree of bending (I–III; Chart I).

The bonding situations I and II are well represented in binuclear complexes containing main-groups and f orbital metals,[2] but only a few examples of the type III have been reported: $[Cp_2Ti(C{\equiv}CSiMe_3)]_2$,[3] $[(COD)Ir(C{\equiv}CSiMe_3)]_2$,[4] and $[(MeCp)_2Zr(C{\equiv}CPh)_2]$.[5] Interestingly, the titanium derivative having a stoichiometry similar to that of the Zr one seems to give initially the binuclear complex with two bridging acetylides but spontaneously undergoes an oxidative coupling at C_α of the acetylide ligands to form (μ-(1–3)η:(2–4)η-*trans*,*trans*-1,4-diphenylbutadiene)bis(bis(η^5-methylcyclopentadienyl)titanium).[6,7] A similar coupling of phenylethynyl ligands has recently been re-

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