Molecular Structure of Trisilylmethane and Synthesis of 1,1,1-Trisilylethane

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Received March 7, 1991

Key Words: Trisilylmethane / 1,1,1-Trisilylethane / CVD feedstock gases / Silicon carbide, hydrogenated, amorphous (a-SiC:H)

As a precursor for trisilyl*methane*, tris(phenylsilyl)methane is prepared by a Merker-Scott reaction of chlorophenylsilane, bromoform, and magnesium turnings in boiling tetrahydrofuran. Chlorophenylsilane is formed in a new synthesis starting from phenylsilane and hydrogen choride/$AlCl_3$ in diethyl ether. The gas phase structure of trisilylmethane $(H_3Si)_3CH$, obtained from $(PhSiH_2)_3CH$ via $(BrSiH_2)_3CH$, has been determined by electron diffraction. Data refinement confirmed a model of C_3 molecular symmetry, with local C_{3v} symmetry for the silyl groups. – As a precursor for 1,1,1-trisilyl*ethane*, 1,1,1-tris(phenylsilyl)ethane has been prepared similarly from chlorophenylsilane, 1,1,1-trichloroethane and magnesium and converted via 1,1,1-tris(bromosilyl)ethane into $CH_3C(SiH_3)_3$.

Hydrogenated amorphous silicon carbide (a-SiC:H) has attracted growing research interest in recent years owing to its use in a wide range of electronic applications, especially photovoltaic devices with energy gaps >2.0 eV. Films of this type are usually formed in plasma enhanced chemical vapour depositon processes (PE-CVD) from a SiH_4 feedstock gas containing CH_4 or other volatile hydrocarbons. The optoelectrical qualities of these alloys are still somewhat unsatisfactory and inferior to those of layers of pure amorphous silicon (a-Si:H)[1].

Recent investigations have shown that the optoelectrical properties of a-SiC:H layers depend on the nature of incorporation of the carbon atoms into the amorphous framework[2,3]. Due to the very different bond energies in SiH_4 and CH_4, CVD processes of mixtures of these gases yield alloys containing a large number of methyl groups, which cause disintegration of the amorphous network. A new approach to obtaining layers with an improved efficiency is directed towards the application of volatile organosilanes having few or no CH bonds as CVD feedstock gases. The most promising candidates are the polysilyl*methane* $H_{4-n}C(SiH_3)_n$ series. CVD experiments with methylsilane, CH_3SiH_3, have shown only moderate success[2], but more recent investigations with disilyl*methane*, $H_2C(SiH_3)_2$, and trisilyl*methane*, $HC(SiH_3)_3$, have led to a-SiC:H films of improved photoelectrical quality[3].

For some time, existing synthetic pathways for both gases were unattractive because of their multistep concept and low yields[4]. More recently a new preparative strategy was tested successfully for the synthesis of di- and trisilylmethane, $HC(SiH_3)_3$, and tetrasilyl*methane*, $C(SiH_3)_4$[5–7]. We report on further improvements of this synthesis and on the determination of the molecular structure of trisilylmethane by electron diffraction. 1,1,1-Trisilyl*ethane*, $CH_3C(SiH_3)_3$, is obtained by a similar series of synthetic steps. This molecule is of interest with regard to our continuing systematic studies of polysilylated ethynes, ethylenes[8,9] and ethanes[10] including, e.g., 1,1-*di*silyl*ethane*[11].

Improved Synthesis of Trisilylmethane

Chlorophenylsilane is a key compound for many Merker-Scott type reactions. It is found to be readily available by chlorination of phenylsilane with $HCl/AlCl_3$ in diethyl ether (Eq. 1). The remaining steps of the trisilylmethane synthesis are represented by Eq. (2)–(4).

$$PhSiH_3 + HCl \longrightarrow PhSiH_2Cl + H_2 \quad (1)$$

$$CHBr_3 + 3\,Mg + 3\,PhSiH_2Cl \longrightarrow (PhSiH_2)_3CH + 3\,MgBrCl \quad (2)$$

$$HC(SiH_2Ph)_3 + 3\,HBr \longrightarrow HC(SiH_2Br)_3 + 3\,PhH \quad (3)$$

$$HC(SiH_2Br)_3 \xrightarrow{LiAlH_4} HC(SiH_3)_3 \quad (4)$$

Molecular Structure of Trisilylmethane

The gas-phase molecular structure of trisilylmethane has been determined by electron diffraction studies. Satisfactory refinement of structural parameters can be achieved assuming C_3 symmetry for the molecule and C_{3v} symmetry for the silyl groups. If the silyl groups are allowed to tilt away from each other ("silyl tilt"), refinement of the tilt leads to an increase to around 6 to 7°, and at the same time the amplitude of vibration for the C(Si)H distances becomes too small. Such a tilt is clearly unreasonable, as the shortest H–H distance between the SiH_3 groups and the unique hydrogen is shorter than the shortest distance between the SiH_3 groups. The tilt is therefore fixed to zero, so that the $CSiH_3$ groups are constrained to have C_{3v} symmetry.

The "silyl twist" of 21.7° corresponds to the dihedral angle H–Si–C–H with a staggered conformation as the refer-

Chem. Ber. **124** (1991) 1953–1956 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1991 0009–2940/91/0909–1953 $ 3.50+.25/0

ence (zero dihedral angle). It is this twist which is responsible for the lowering of the molecular symmetry from C_{3v} to C_3. The molecular structure of the compound is shown in Figure 1.

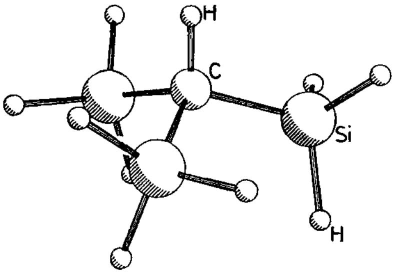

Figure 1. Molecular structure of trisilylmethane

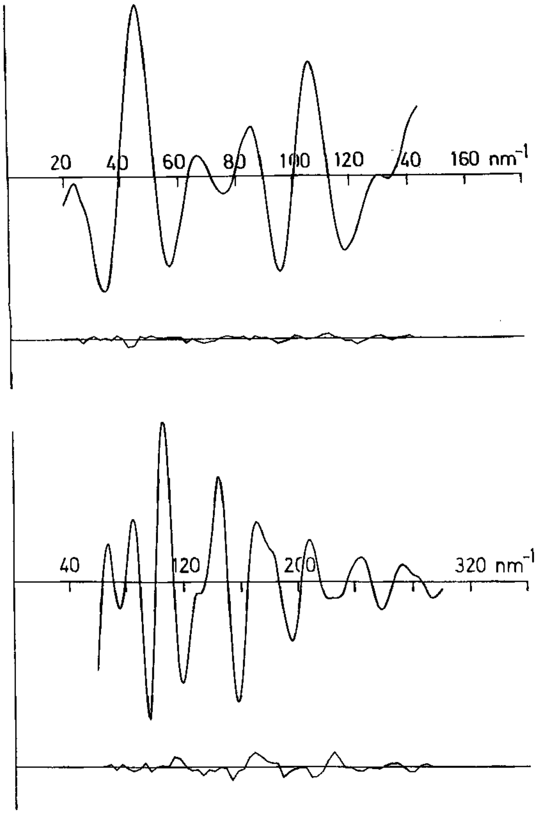

Figure 2. Observed and final weighted difference molecular scattering intensities for nozzle-to-plate distances of a) 286.0 mm and b) 128.2 mm

Pertinent observed and final weighted difference molecular scattering intensities for the two nozzle-to-plate distances are given in Figure 2a, b, and observed and difference radial distribution curves in Figure 3. The bond distances are very similar to those determined for tetrasilylmethane[7] and tetramethylsilane[12] indicating that these molecules are virtually strain-free and not seriously crowded species. This result is at variance with predictions in a theororetical paper, in which $C(SiH_3)_4$ was even assumed to be unstable owing to steric congestion[13]. The lack of steric strain is also demonstrated by the very small widening of the SiCSi angles from the tetrahedral value.

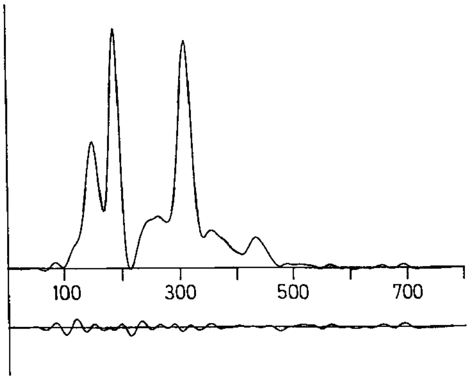

Figure 3. Observed and difference radial distribution curves $P(r)/r$. Before Fourier inversion the data were multiplied by $s \cdot \exp(-0.00002\, s^2)/(Z_{Si} - f_{Si})(Z_C - f_C)$

Synthesis of 1,1,1-Trisilylethane

1,1,1-Trisilylethane has been prepared by a method similar to that used for trisilylmethane. The reaction of chlorophenylsilane with 1,1,1-trichloroethane under Merker-Scott conditions, using magnesium turnings in refluxing THF, leads to 1,1,1-tris(phenylsilyl)ethane in low yield (Eq. 5).

$$CH_3CCl_3 + 3\ Mg + 3\ PhSiH_2Cl \rightarrow CH_3C(SiH_2Ph)_3 + 3\ MgCl_2 \quad (5)$$

This poor yield is a result of an incomplete in situ Grignard reaction between CH_3CCl_3 and magnesium, which leads to the formation of significant amounts of only partially silylated compounds, $CH_3C(Cl)(SiH_2Ph)_2$ and $CH_3C(Cl)_2(SiH_2Ph)$. Transmetallation reactions lead to the byproducts $CH_3C(H)(SiH_2Ph)_2$ and $CH_3C(H)_2(SiH_2Ph)$ detected also in the product mixture. 1,1,1-Tris(phenylsilyl)ethane is an air-stable colourless solid (m.p. 80°C), which is easily identified by standard analytical methods (see Experimental).

Treatment of 1,1,1-tris(phenylsilyl)ethane with pure hydrogen bromide at −78°C according to the method of Fritz and Kummer[14] affords 1,1,1-tris(bromosilyl)ethane in nearly quantitative yield as a colourless liquid (b.p. 64°C/0.15 Torr), which is very sensitive to air moisture (Eq. 6).

$$CH_3C(SiH_2Ph)_3 + 3\ HBr \longrightarrow CH_3C(SiH_2Br)_3 + 3\ PhH \quad (6)$$

$$CH_3C(SiH_2Br)_3 \xrightarrow{LiAlH_4} CH_3C(SiH_3)_3 \quad (7)$$

Reduction of $CH_3C(SiH_2Br)_3$ with $LiAlH_4$ leads to 1,1,1-trisilylethane in good yield (Eq. 7). To avoid cleavage of the Si−C linkages in trisilylethane the reaction has to be accomplished in a two-phase system using a phase-transfer catalyst, as outlined previously. Under these reaction conditions only traces of monosilane are produced[5−7,15].

1,1,1-Trisilylethane is a colourless liquid, b.p. 75°C, which solidifies at −8 ± 2°C. It is surprisingly stable to moisture and air. The spectroscopic data are in agreement with the proposed constitution (see Experimental). There is no evidence for an isomerisation or dismutation of this compound to give e. g. 1,1,2-trisilylethane.

Theoretical studies have suggested that $CH_3C(SiH_3)_3$ is thermodynamically of only limited stability ($H_{f\,calc.} = -6.5$ kcal/mol). It may therefore have advantages as a feedstock gas for the deposition of amorphous or crystalline silicon carbide films[16].

This work was supported by the *Deutsche Forschungsgemeinschaft* (Leibniz-Programm), by the *Fonds der Chemischen Industrie*, and by the *European Community* [EN3S-0059-D (B)]. We thank Mr. *U. Flessner* and Ms. *U. Volkhardt* for GC/MS investigations and *Wacker-Chemie*, Burghausen, for the donation of chemicals.

Experimental

General: All experiments were carried out under pure dry nitrogen. Solvents were purified, dried and kept under nitrogen. – NMR: C_6D_6 as solvent and tetramethylsilane as reference compound in all cases (Bruker WP 100 SY, Jeol GX 270, Jeol GX 400 spectrometers). – IR: films between KBr plates (Nicolet FT 5 DX spectrophotometer). – Gas chromatography: columns SIL 5, Hewlett Packard GC 5890 A instrument with a mass-sensitive detector MSD 5970 (EI, 70 eV). – Phenylsilane was prepared by $LiAlH_4$ reduction of commercially available trichlorophenylsilane. Trisilymethane was prepared as published previously[5].

Chlorophenylsilane: A solution of 184.0 g (1.7 mol) of phenylsilane in 150 ml of diethyl ether was saturated with dry HCl gas at room temperature. Addition of a small quantity of $AlCl_3$ led to vigorous H_2 evolution. While the reaction was in progress, a slow stream of HCl was passed through the solution, and occasionally more $AlCl_3$ was added such that there was always some solid catalyst present in the reaction mixture. When the evolution of hydrogen had ceased (ca. 24 h), the solvent was removed under reduced pressure. Distillation of the remaining liquid yielded 216.0 g (89%) of chlorophenylsilane, b.p. 58°C/14 Torr. – ^1H NMR: $\delta = 5.05$ [s, SiH, J(SiH) = 236 Hz], 7.3 (m, Ph). – MS: m/z = 144–141 [C_6ClSiH_x], 107–105 [C_6SiH_x], 79–77 [C_4SiH_x], 65/63 [ClSi].

1,1,1-Tris(phenylsilyl)ethane: A solution of 25.9 g (0.19 mol) of 1,1,1-trichloroethane in 400 ml of tetrahydrofuran was added dropwise (ca. 14 h) to a mixture of 86.5 g (0.61 mol) of chlorophenylsilane and 16.2 g (0.67 mol) of magnesium turnings in 500 ml of refluxing THF. After completion of the addition and a further reflux period of 4 h, the mixture was poured onto crushed ice, neutralised with sodium hydrogencarbonate and filtered. The organic layer was dissolved in 200 ml of hexane, the solution washed twice with water and dried with magnesium sulphate. Solvents and volatile reaction products were removed in vacuo by heating the mixture to 130°C. The remaining yellow liquid was dissolved in 50 ml of ethanol and neutralised with sodium hydrogencarbonate. After filtration 3.0 g (4.3%) of 1,1,1-tris(phenylsilyl)ethane crystallised at –10°C as a white solid, that was recrystallised from absolute ethanol, m.p. 80°C. – ^1H NMR: $\delta = 1.31$ (s, CH_3), 4.67 (s, SiH_2), 7.06–7.48 (m, Ph). – ^{13}C NMR: $\delta = -8.96$ [m, J(SiC) = 37.7 Hz, $C_{centr.}$], 16.29 [qm, J(CH) = 130 Hz, CH_3], 128.27 (dd, C-3/C-5), 130.34 (dt, C-4), 131.23 (m, C-1), 136.67 (dm, C-2/C-6): J(CH) ≈ 160, J(CCCH) = 9 Hz. – ^{29}Si NMR: $\delta = -23.9$ [tm, J(SiH) = 197.6 Hz]. – IR (film): $\tilde{\nu}$ = 3068 cm^{-1} m, 3050 m, 3012 w, 2947 m, 2923 w, 2864 w, 2123 s, 1455 m, 1427 s, 1116 s, 1096 m, 1077 m, 1067 m, 1038 m, 1011 m, 998 m, 936 s, 927 s, 859 s, 854 s b, 796 s, 734 s, 711 s, 698 s, 597 s, 656 m, 491 w, 481 w, 468 w, 450 w. – MS: m/z = 350–348 [$C_{20}Si_3H_x$], 272–266 [$C_{14}Si_3H_x$], 242–237 [$C_{14}Si_2H_x$], 213–208 [$C_{14}SiH_x$], 194–192 [$C_8Si_3H_x$], 163–161 [$C_8Si_2H_x$], 136–131 [C_8SiH_x], 107–105 [C_6SiH_x].

1,1,1-Tris(bromosilyl)ethane: A five- to sevenfold molar excess of dry hydrogen bromide was condensed into a cooling trap containing 2.7 g (7.7 mmol) of 1,1,1-tris(phenylsilyl)ethane at –196°C. The reaction mixture was stirred at –78°C over night. Excess HBr was evaporated by warming the solution to room temperature. Benzene was removed from the reaction mixture in vacuo to leave 2.6 g of 1,1,1-tris(bromosilyl)ethane (quantitative yield), b.p. 64°C/0.15 Torr. – ^1H NMR: $\delta = 1.33$ (s, CH_3), 4.63 (s, SiH_2). – ^{13}C NMR: $\delta = -2.0$ [m, $C_{centr.}$, J(SiC) = 41.2 Hz], 13.2 [q · sept, CH_3, J(CH) = 132.8, J(CCSiH) = 3 Hz]. – ^{29}Si NMR: $\delta = -16.6$ [tm, J(SiH) = 247.3 Hz]. – MS: m/z = 363–345 [$C_2Si_3Br_3H_x$], 283–274 [$C_2Si_3Br_2H_x$], 250–241 [$C_2Si_2Br_2H_x$], 171–165 [$C_2Si_2BrH_x$], 141–133 [C_2SiBrH_x], 109/107 [SiBr], 61–55 [C_2SiH_x].

1,1,1-Trisilylethane: 2.3 g (6.4 mmol) of 1,1,1-tris(bromosilyl)ethane was added to a suspension of 1.8 g (47 mmol) of $LiAlH_4$ and 0.25 g (1.1 mmol) of benzyltriethylammonium chloride in 50 ml of 1,2,3,4-tetrahydronaphthalene. The reaction mixture was stirred at room temp. for 20 h and at 60°C for 2 h. Under reduced pressure the product was condensed into a Schlenk tube cooled in liquid nitrogen through a condenser cooled to 10°C, the temp. of the reaction flask being slowly increased from room temp. to 60°C. After thawing the Schlenk tube to room temp., small amounts of SiH_4 produced in the reaction were removed in a slow stream of nitrogen. The silane was passed through a Hg bubbler and ignited in air. Impurities of tetralin were removed by fractional condensation to yield 0.5 g (65%) of 1,1,1-trisilylethane, b.p. 75°C, m.p. –8 ± 2°C. – ^1H-NMR: $\delta = 1.34$ (s, 3H, CH_3), 3.74 (s, 9H, SiH_3). – ^{13}C NMR: $\delta = -19.20$ [q · dez, not resolved, $C_{centr.}$, J(SiC) = 39.7 Hz], 20.44 [q · dez, CH_3, J(CH) = 133.5, J(CCSiH) = 3 Hz]. – ^{29}Si NMR: $\delta = -44.2$ [qm, J(SiH) = 199.5 Hz]. – IR (film): $\tilde{\nu}$ = 2952 cm^{-1} w, 2935 w, 2922 w, 2899 w, 2859 w, 2144 s, 1450 m, 1078 m, 1020 w, 938 s, 902 s, 826 s, 680 m. – MS: m/z = 121–113 [$C_2Si_3H_x$], 92–84 [$C_2Si_2H_x$], 74–69 [CSi_2H_x], 62–55 [C_2SiH_x], 45–43 [$CSiH_x$], 31–28 [SiH_x].

Electron Diffraction: Electron diffraction scattering data were recorded on Kodak Electron Image photographic plates by using the Edinburgh gas diffraction apparatus[17], with the sample and nozzle held at room temp. (20°C). The accelerating voltage was 44.5 kV. Three plates were obtained at the long camera distance (286.0 mm) and three at the short distance (128.2 mm), and data were also recorded for benzene to provide calibration of the nozzle-to-plate distances and electron wavelength. Plates were traced on a Joyce-Loebl MDM6 microdensitometer[18] at the S.E.R.C. Laboratory, Daresbury. Data reduction[18] and least-squares refinements[19] were performed by using standard programs and scattering factors[20]. Parameters used to define the off-diagonal weight matrices used in

Table 1. Molecular parameters, (r_g, distances [Å], angles [°]) of trisilylmethane. Note: Errors quoted in this and the following tables are estimated standard deviations, increased to allow for systematic errors

p_1	r(C–H)	1.100 (fixed)
p_2	r(C–Si)	1.878(1)
p_3	r(Si–H)	1.497(3)
p_4	<(HCSi)	107.8(2)
	<(SiCSi)	111.0(2)
p_5	<(CSiH)	108.7(7)
p_6	SiH_3 twist	21.7(18)
p_7	SiH_3 tilt	0.000 (fixed)

Table 2. Weighting functions and other experimental data pertinent to the electron diffraction structure determination of trisilylmethane

Height [nm]	Δs	s_{min}	sw_1 [nm^{-1}]	sw_2	s_{max}
285.96	0.2	2.0	4.0	12.2	14.4
128.23	0.4	6.0	8.0	26.0	30.0

Height [mm]	Correlation parameter	Scale factor	Electron wavelength [Å]
285.96	0.3340	0.726(7)	0.05660
128.23	0.4285	0.819(18)	0.05661

Table 3. Interatomic distances [Å] and amplitudes of vibration [Å] of trisilylmethane

r_1	C−H	1.100	0.070 (fixed)
r_2	C−Si	1.878(1)	0.051(2)
r_3	Si−H	1.497(3)	0.105(3)
r_4	H···Si	2.450(3)	0.089(12)
r_5	C···H	2.752(8)	0.113(11)
r_6	C···H	2.752(8)	0.113 (tied to u_5)
r_7	C···H	2.752(8)	0.113 (tied to u_5)
r_8	Si···Si	3.096(1)	0.099(2)
r_9	H···H	2.456(9)	0.150 (fixed)
r_{10}	Si···H	3.706(21)	0.228(20)
r_{11}	Si···H	4.339(7)	0.109(8)
r_{12}	Si···H	3.205(14)	0.250 (fixed)
r_{13}	Si···H	3.239(14)	0.250 (fixed)
r_{14}	Si···H	3.659(21)	0.228 (tied to u_{10})
r_{15}	Si···H	4.354(6)	0.109 (tied to u_{11})

Table 4. Least-squares correlation matrix (· 100). Note: Only elements with absolute values above 50 are listed

	p_4	u_5	k_2
p_2	79		
u_4		52	
u_2			66
u_8			63

the refinement are given in Table 1 together with other experimental data. The geometrical parameters obtained in the refinements are listed in Table 2, while Table 3 gives interatomic distances and vibrational parameters, and Table 4 contains the most significant elements of the least-squares correlation matrix.

CAS Registry Numbers

$PhSiH_3$: 694-53-1 / $PhSiH_2Cl$: 4206-75-1 / CH_3CCl_3: 71-55-6 / $CHBr_3$: 75-25-2 / $CH_3C(SiH_2Ph)_3$: 133753-57-8 / $(PhSiH_2)_3CH$: 121232-83-5 / $CH_3C(SiH_2Br)_3$: 133753-58-9 / $HC(SiH_2Br)_3$: 121232-84-6 / $CH_3C(SiH_3)_3$: 78570-63-5 / $HC(SiH_3)_3$: 4335-85-7

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[1] [1a] W. Paul, D. K. Paul, B. von Roedern, J. Blake, S. Oguz, *Phys. Rev. Lett.* **46** (1981) 1016. — [1b] A. Moromoto, T. Miura, M. Kumeda, T. Shimizu, *Jpn. J. Appl. Phys.* **20** (1981) L 833. — [1c] D. E. Carlson, *IEEE Transactions On Electron Devices* **36** (1989) 2775. — [1d] S. Wiedemann, M. Smoot, B. Fieselmann, *Appl. Phys. Lett.* **54** (1989) 1537.

[2] D. P. Tanner, G. R. Johnson, M. D. Sefcik, *Solar Energy Mater.* **3** (1980) 533; A. Matsuda, T. Yamaoka, S. Wolff, M. M. Koyama, Y. Imanishi, H. Kataoka, H. Matsuura, K. Tanaka, *J. Appl. Phys.* **60** (1986) 4025; A. Bubenzer, M. Gorn, N. Kniffler, K. Thalheimer, G. Winterling in *Status Report 1987 — Photovoltaic* (R. Urban, Ed.), S. 349, PBE-Kernforschungsanlage Jülich 1988.

[3] [3a] W. Beyer, R. Hager, H. Schmidbaur, G. Winterling, *Appl. Phys. Lett.* **54** (1989) 1666. — [3b] Solarex Corporation (C. R. Dickson, Inv.), Eur. Pat.-Anmeldung 0.233.613 (1987). — [3c] B. Fieselmann, M. Milligan, A. Wilczynski, J. Pickens, C. R. Dickson, *19th IEEE Photovoltaic Specialists Conference*, New Orleans 1987, Abstr. 19; *IEEE* **1987**, 1510.

[4] H. Schmidbaur, J. Ebenhöch, *Z. Naturforsch., Teil B*, **41**(1986) 1527.

[5] R. Hager, O. Steigelmann, G. Müller, H. Schmidbaur, *Chem. Ber.* **122** (1989) 2115.

[6] J. Zech, H. Schmidbaur, *Chem. Ber.* **123** (1990) 2087.

[7] R. Hager, O. Steigelmann, G. Müller, H. Schmidbaur, H. E. Robertson, D. W. H. Rankin, *Angew. Chem.* **102** (1990) 204; *Angew. Chem. Int. Ed. Engl.* **29** (1990) 201.

[8] H. Schmidbaur, J. Ebenhöch, G. Müller, *Z. Naturforsch., Teil B*, **42** (1987) 142.

[9] H. Schmidbaur, J. Ebenhöch, G. Müller, *Z. Naturforsch., Teil B*, **43** (1988) 49.

[10] H. Schmidbaur, C. Dörzbach, *Z. Naturforsch. Teil B*, **42** (1987) 1088.

[11] H. Schmidbaur, R. Hager, *Z. Naturforsch. Teil B*, **43** (1988) 571.

[12] B. Beagley, J. J. Monaghan, T. G. Hewitt, *J. Mol. Struct.* **8** (1971) 401.

[13] J. J. Toman, A. A. Frost, S. Topiol, S. Jacobson, M. A. Ratner, *Theoret. Chim. Acta (Berlin)* **58** (1981) 285.

[14] G. Fritz, D. Kummer, *Z. Anorg. Allg. Chem.* **308** (1961) 105.

[15] [15a] Y. Goldberg, V. Dirnens, E. Lukevics, *J. Organomet. Chem. Lib.* **20** (1988) 211. — [15b] V. N. Gevorgyan, L. M. Ignatovich, E. Lukevics, *J. Organomet. Chem.* **284** (1985) C31. — [15c] V. N. Gevorgyan, E. Lukevics, *J. Chem. Soc., Chem. Commun.* **1985**, 1234. — [15d] H. Schmidbaur, J. Rott, *Z. Naturforsch., Teil B*, **45** (1990) 961.

[16] H. E. O'Neal, M. A. Ring, *J. Organomet. Chem.* **213** (1981) 419.

[17] C. M. Huntley, G. S. Laurenson, D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.* **1980**, 954.

[18] S. Cradock, J. Koprowski, D. W. H. Rankin, *J. Mol. Struct.* **77** (1981) 113.

[19] A. S. F. Boyd, G. S. Laurenson, D. W. H. Rankin, *J. Mol. Struct.* **71** (1981) 217.

[20] M. Fink, A. Ross, *International Tables for X-ray Crystallography*, International Union of Crystallography, Reidel, Dordrecht, in press.

[108/91]