Compounds of Germanium and Tin, 21[◇]

A Tetraaryldigermene with a Short Germanium–Germanium Double Bond and a Nearly Planar Environment of Both Germanium Atoms☆

Manfred Weidenbruch*, Martin Stürmann, Hartmut Kilian, Siegfried Pohl†, and Wolfgang Saak

Fachbereich Chemie der Universität Oldenburg,
Carl-von-Ossietzky-Straße 9–11, D-26111 Oldenburg, Germany

Received December 16, 1996

Keywords: Germanium / Digermenes / Tin / Germylenes / Stannylenes

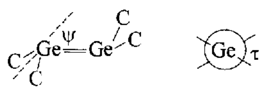
---

Treatment of $GeCl_2 \cdot$ dioxane with the Grignard reagent RMgBr (R = 2-*t*Bu-4,5,6-Me_3C_6H) furnishes the tetraaryldigermene $R_2Ge{=}GeR_2$ (**8**). X-ray structure-analysis of **8** reveals a short Ge=Ge double bond, a nearly planar environment of both germanium atoms and extremely widened C–Ge–C angles of 128°. In solution, **8** dissociates into two germylene molecules R_2Ge: which can be trapped with oxygen or by [4 + 1] cycloaddition reactions with 1,4-dihetero-1,3-dienes. A similar cycloadduct of a stannylene was obtained by thermolysis of $(R'_2Sn)_3$ (R' = 2,4,6-*i*$Pr_3C_6H_2$), in the presence of a 1,4-diazabutadiene and characterized by an X-ray structure-analysis.

The double-bond system of alkenes is usually characterized by a planar arrangement of the substituents. Twisting of the C=C double bond can only occur in the presence of very bulky groups. However, homonuclear double bonds between the heavier homologues of carbon exhibit a different behaviour and, in particular, digermenes and distannenes show marked *trans* folding of the substituents[2]. Thus, for example, *trans* bent angles ψ of 35 to 47° have been calculated for $H_2Ge{=}GeH_2$, the parent compound of the digermenes[3–7]. Such calculations are corroborated by experiment: X-ray-crystallographic studies of the tetraalkyl- and tetraaryldigermenes **1**–**3** have in each case revealed some degree of *trans* pyramidalization where, in addition, a slight twisting of the double bond by the angle τ may also occur in order to reduce the steric overcrowding (Scheme 1)[3,8–10].

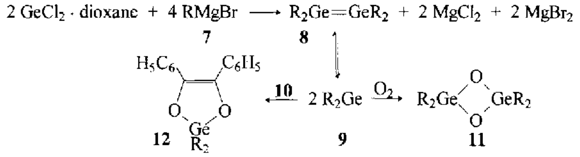
Scheme 1

$RR'Ge{=}GeR'R$



Compound	Ge=Ge [pm]	Ψ [°]	τ [°]	C–Ge–C [°]	Ref.
1 (R = R' = 2,6-$Et_2C_6H_3$)	221.3(2)	12	10	115.4(2)	[8]
2 [R = R' = $CH(SiMe_3)_2$]	234.7(2)	32	0	112.5(2)	[3, 9]
(*Z*)-**3** (R = 2,4,6-$Me_3C_6H_2$, R' = 2,6-*i*$Pr_2C_6H_3$)	230.1(1)	36	7	109.9(2)	[10]

Very recently, Kira et al. reported the preparation of the persilylated digermenes $(R_3Si)_2Ge{=}Ge(SiR_3)_2$, [$R_3Si$ = *i*Pr_2MeSi (**4**), *t*$BuMe_2Si$ (**5**), *i*Pr_3Si (**6**)] and the structural analyses of the compounds **4** and **6**[11]. The observed, rather small *trans* bent angles of 6.5 and 16.4° were assumed to be due mainly to electronic effects and result in an almost planar environment about the Ge=Ge double bond[11].



R = 2-*t*Bu-4,5,6-Me_3C_6H

We have now found that a similar planar arrangement of the substituents about the Ge=Ge double bond is not only realized with electropositive groups, but can also be achieved in a tetraaryldigermene by judicious choice of the *ortho*-alkyl groups. Thus, the reaction of the germanium(II) chloride · dioxane adduct with the Grignard reagent **7** resulted in the formation of the digermene **8**, which was isolated in good yield in the form of orange-yellow, air-sensitive crystals. An X-ray crystal-structure analysis of **8** revealed some interesting features (Figure 1).

The steric influence of the bulky *ortho-tert*-butyl groups does not lead to a stretching of the Ge=Ge double bond as is the case in compounds **2** and **3**. Instead, the system responds to possible interactions between these groups by a twisting of τ = 20.4°. The short germanium-germanium separation of 225.2 pm is also surprising when one considers that the analogously substituted distannene R_2SnSnR_2 exhibits a very large tin-tin separation, which is appreciably larger than even a normal tin-tin single-bond length[12]. Even more unusual are the completely planar environments of both germanium atoms, the two *ipso*-carbon atoms and the respective other germanium atom being exactly coplanar (angular sums in each case 360°).

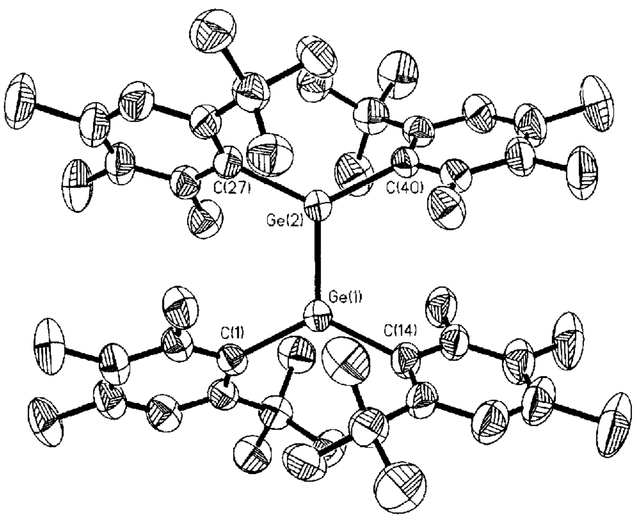
On the other hand, the largest displacement parameters $U_{22}(Ge) = 84\ pm^2 > 1/2(U_{11} + U_{33}) = 38\ pm^2$ can lead to

---

[◇] Part 20: Ref.[1].

0009-2940/97/0606–0735 $ 17.50+.50/0

Figure 1. ORTEP drawing of compound **8** (50% probability, hydrogen atoms omitted)[a]



[a] Selected bond lengths [pm] and angles [°]: Ge(1)–Ge(2) 225.21(8), Ge(1)–C(1) 201.1(5), Ge(1)–C(14) 200.8(5), Ge(2)–C(27) 201.2(5), Ge(2)–C(40) 201.9(5); C(14)–Ge(1)–C(1) 128.0(2), C(1)–Ge(1)–Ge(2) 116.1(2), C(14)–Ge(1)–Ge(2) 116.0(2), C(27)–Ge(2)–C(40) 128.5(2), C(27)–Ge(2)–Ge(1) 115.0(2), C(40)–Ge(2)–Ge(1) 116.6(2).

an alternative anisotropic dislocation of both germanium atoms from the ideal $C_2Ge{=}GeC_2$ plane. By using $\hat{u} = [U_{22} - 1/2(U_{11} + u_{33})]^{1/2} = 6.8$ pm or $\sqrt{U_{22}} = 9.2$ pm one obtains *trans* fold angles of 7.9 and 10.4°, respectively. The anisotropic behaviour of the germanium atoms in the crystal should be interpreted in terms of a orientation disorder in which the dislocations of +/– and –/+ appear by an equal frequency[20].

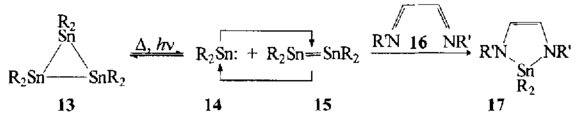
Also surprising are the C–Ge–C bond angles of 128°, which are considerably more widened than those in other compounds investigated to date. This angle widening cannot be attributed to steric effects since the even more overcrowded compound R_2Ge: with R = 2,4,6-tBu$_3$C$_6$H$_2$ exhibits a C–Ge–C angle of only 108.0° and, furthermore, does not form a digermene in the solid state[13]. When we compare compound **8** with, for example, (*Z*)-**3**, which bears substituents with similar steric requirements, it is clear that the structure of (*Z*)-**3** closely approaches the theoretically predicted results, whereas the structural parameters of **8** are closer to those of an alkene. At present, we cannot provide a satisfactory explanation for this phenomenon.

The behaviour of the digermenes in solution is just as unpredictable as their structure in the solid state. While tetraaryldigermenes retain their structural integrity in solution, compound **2** dissociates into two germylene molecules[2]. The situation with the persilylated compounds **4**–**6** is still uncertain, although some of their reactions are indicative of retention of the Ge=Ge double bond in solution[11].

The findings for the digermene **8** are also contradictory. On the one hand, the position and intensity of the longest wavelength absorption in the electronic spectrum correspond with the bands observed in the spectra of other digermenes, thus suggesting the existence of digermene units in solution. On the other hand, the mass spectrum and cryoscopic molecular-mass determinations suggest that **8** dissociates into two germylene molecules **9**, both in the gas phase and in solution. Attempts to confirm the existence of either **8** or **9** in solution by trapping reactions with, for example, 2,3-dimethylbutadiene or the heavier chalcogens sulfur, selenium and tellurium, have not yet provided any unambiguous results. However, the reaction with oxygen was successful and furnished the isolable 2,4-digerma-1,3-dioxetane **11**. 1,4-Dihetero-1,3-dienes also reacted with the germylene **9** to provide [4 + 1] cycloaddition products. For example, in the case of benzil (**10**), compound **12** was obtained.

The implication of the latter result, that the germylene **9** is the principal component in solution, is indirectly supported by analogous observations in silicon chemistry. Thus, photolyses of hexa-*tert*-butylcyclotrisilane – concomitantly giving rise to both di-*tert*-butylsilylene and tetra-*tert*-butyldisilene – in the presence of benzil or diazabutadienes, result in the exclusive formation of the highly strained [4 + 2] cycloaddition products of the 1,4-dihetero-1,3-dienes with the disilene, and not strain-free [4 + 1] cycloadducts[14]. Since the extremely stretched Si–Si bond length in the [4 + 2] adduct and the Ge–Ge separation in corresponding products formed from the digermene **8** and the 1,4-diheterodienes should be comparable, a [4 + 2] adduct rather than a [4 + 1] adduct would also be expected if the digermene **8** were to exist in solution.

In order to supplement the series of 1,4-diazabutadiene cycloadducts, we also heated the diene **16** with the cyclotristannane **13** which, upon photolysis or thermolysis, furnishes predominantly the distannene **15** with only traces of the stannylene **14**[15–17]. Compound **15**, as confirmed by ^{119}Sn-NMR data[15] and trapping reactions[16–17], is the only currently known distannene that remains its structural integrity in solution. The reaction of **13** with **16** smoothly furnished the [4 + 1] cycloaddition product **17**, the structure of which was confirmed by analysis, spectra data and X-ray crystallography (Figure 2).

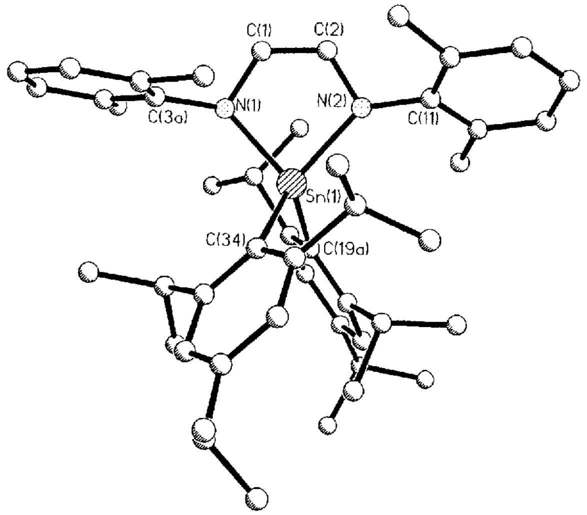


R = 2,4,6-iPr$_3$C$_6$H$_2$; R' = 2,6-Me$_2$C$_6$H$_3$

Structural analysis of the adduct **17** reveals a planar five-membered ring and no other features worthy of note, except for a somewhat stretched Sn–N bond length of 207 pm and an acute N–Sn–N angle of 84°. The preferential formation of **17** over a [4 + 2] cycloaddition product from **15** and **16** is not surprising since the Sn–Sn bond is markedly longer than the Si–Si or Ge–Ge bonds and would give rise to an extremely distorted and thus unstable six-membered ring system.

Financial support of our work by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* is gratefully acknowledged.

Figure 2. Molecular structure of compound **17** in the crystal (hydrogen atoms omitted)



Experimental Section

All manipulations were performed under dry nitrogen and argon by using Schlenk techniques. Solvents were purified, dried and distilled under argon. – ^1H and ^{13}C NMR: Bruker AM 300. – MS: Varian MAT 212. – UV/Vis: ComSpec with fibre optics. – Elemental analyses: Analytische Laboratorien, D-51779 Lindlar, Germany.

Tetrakis(2-tert-butyl-4,5,6-trimethylphenyl)digermene (**8**) *and Bis(2-tert-butyl-4,5,6-trimethylphenyl)germylene* (**9**): To a stirred solution of approx. 8.7 mmol of the Grignard compound **7** [prepared from 2.23 g (8.74 mmol) of 1-bromo-2-*tert*-butyl-4,5,6-trimethylbenzene and 0.50 g (20.6 mmol) of magnesium turnings in 40 ml of THF] at −18 °C, a solution of 1.0 g (4.3 mmol) of germanium(II) chloride · dioxane in 20 ml of THF was added dropwise over a period of 20 min. The mixture was then allowed to warm to room temp., the solvent was removed, and the residue was extracted with 200 ml of toluene. The magnesium salts were filtered off, the solution was concentrated to a volume of 70 ml, and cooled to −18 °C to furnish 1.33 g(73% yield) of yellow-orange crystals of **8**, m. p. 150 °C. – $C_{52}H_{76}Ge_2$ (846.4): calcd. C 73.79, H 9.05; found C 73.67, H 8.96. – Spectroscopic data for **9**: H NMR (C_6D_6, 25°C): δ = 1.61 (s, 18H), 1.82 (s, 6H), 2.19 (s, 6H), 2.41 (s, 12H), 7.29 (s, 2H). – ^{13}C NMR (C_6D_6, 25°C): δ = 16.56, 21.20, 27.50, 32.87, 37.47, 133.33, 135.76, 141.93, 146.68, 150.80. – MS (CI, isobutane); *m/z* (%): 425 (100) [M^+]. – UV/Vis: λ_{max} (ε) = 440 nm (7500).

2,2,4,4-Tetrakis(2-tert-butyl-4,5,6-trimethylphenyl)-2,4-digerma-1,3-dioxetane (**11**): Dry oxygen was bubbled slowly through a solution of 0.32 g (0.176 mmol) of **9** in 25 ml of toluene at room temp. until the orange solution became colourless (15 min). The reaction mixture was stirred for 30 min and then concentrated to a volume of 5 ml. The precipitated solid was recrystallized from a minimum amount of *n*-hexane to provide 0.25 g (37% yield) of colourless crystals of **11**, m.p. 224°C. – ^1H NMR (C_6D_6, 25 °C): δ = 1.56 (s, 36H), 1.88 (s, 12H), 2.17 (s, 12H), 2.64 (s, 12H), 7.27 (s, 4H). – ^{13}C NMR (C_6D_6, 25 °C): δ = 16.01, 21.33, 22.91, 33.56, 37.48, 134.25, 136.58, 142.11, 142.67, 151.65. – MS (CI, isobutane); *m/z* (%): 879 (3) [M^+], 439 (53) [$M^+/2$]. – $C_{52}H_{76}Ge_2O_2$ (878.35): calcd. C 71.12, H 8.72; found C 71.27, H 8.82.

2,2-Bis(2-tert-butyl-4,5,6-trimethylphenyl)-4,5-diphenyl-2-germa-1,3-dioxacyclopent-4-ene (**12**): A solution of 0.37 g (0.87 mmol) of **9** and 0.184 g (0.87 mmol) of **10** in 25 ml of toluene was stirred for 1 h. The solvent was then removed in vacuo, the residue was redissolved in 20 ml of *n*-hexane, and the resulting solution was cooled to −20 °C to yield 0.40 g (73% yield) of colourless crystals of **12**, m. p. 176 °C. – ^1H NMR (C_6D_6, 25 °C): δ = 1.62 (s, 18 H), 1.71 (s, 6 H), 2.04 (s, 6 H), 2.24 (s, 6 H), 7.01–7.78 (m, 10 H), 7.26 (s, 2H). – ^{13}C NMR ($CDCl_3$, 25 °C): δ = 15.59, 21.11, 23.88, 32.58, 36.66, 126.64, 127.36, 127.74, 127.85, 133.18, 135.20, 137.18, 137.91, 140.65, 152.45. – MS (CI, isobutane); *m/z* (%): 635 (38) [M^+]. – $C_{40}H_{48}GeO_2$ (633.41): calcd. C 75.85, H 7.64; found C 75.68, H 7.76.

1,3-Bis(2,6-dimethylphenyl)-2,2-bis(2,4,6-triisoporpylphenyl)-1,3-diaza-2-stannacylopent-4-ene (**17**): A solution of 0.50 g (0.32 mmol) of **13** in 50 ml of toluene was heated to 60 °C. At this temp., a solution of 0.25 g (0.95 mmol) of **16** in 20 ml of toluene was added dropwise with stirring. After stirring for 2 h, the initial ruby-red colour of the solution had changed to orange. The toluene was distilled off in vacuo, the residue was dissolved in 50 ml of *n*-pentane, and the solution was filtered. Cooling of the filtrate to −18 °C firstly yielded unreacted **15**, which was filtered off. the remaining solution was concentrated to a volume of 20 ml and again cooled to −18 °C to afford crystals of **17**. For further purification the crystals were recrystallized twice from a minimum amount of *n*-pentane to provide 0.24 g (32% yield) of red, rectangular crystals of **17**, m. p. 108 °C. – ^1H NMR (C_6D_6, 25 °C): δ = 0.98 (d, 24 H, $^3J_{H,H}$ = 6.5 Hz), 1.09 (d, 12 H, $^3J_{H,H}$ = 6.7 Hz), 2.41 (s, 12 H), 2.65 (sept, 2 H), 2.99 (sept, 4 H), 5.84 (s, 2 H), $^3J_{H,^{117/119}Sn}$ = 33 Hz), 6.92 (m, 6 H), 7.01 (s, 4 H, $^4J_{H,^{117/119}Sn}$ = 14 Hz). – ^{13}C NMR (C_6D_6, 25 °C): δ = 21.14, 23.95, 25.09, 34.45, 38.91 ($^3J_{^{13}C,^{117/119}Sn}$ = 71 Hz), 121.16, 151.07, 153.89. – MS (field desorption); *m/z* (%): 790 (100) [M^+]. – $C_{48}H_{66}N_2Sn$ (789.3): calcd. C 73.00, H 8.42, N 3.50; found C 72.94, H 8.35, N 3.57.

X-ray Structural Analyses of Compounds **8** · 2 C_6H_6 *and* **17**: Single crystals were grown from saturated solutions in benzene (**8**) or *n*-pentane (**17**). The structures were solved by direct-phase determination using the SHELXS program system and refined by full-matrix least-squares techniques against F^2 with the SHELX 93 program system[18]. Hydrogen atoms were placed in calculated posi-

Table 1. Crystallographic data of compounds **8** and **17**

	8 · 2 C_6H_6	**17**
formula	$C_{64}H_{88}Ge_2$	$C_{48}H_{66}N_2Sn$
mol. mass	1002.52	798.72
cryst. size [mm]	0.87 × 0.57 × 0.53	0.61 × 0.42 × 0.19
cryst. system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a [pm]	1806.04(11)	1023.80(10)
b [pm]	1738.4(2)	2399.5(3)
c [pm]	1820.07(11)	1806.0(2)
β [°]	91.055(8)	90.71(2)
V [× 10^6 pm^3]	5713.3(7)	4436.3(9)
Z	4	4
$d_{calcd.}$ [g cm^{-3}]	1.166	1.182
diffractometer	Siemens STOE AED 2	
radiation (graphite-monochromated) [pm]	Mo-K_α 71.073	Mo-K_α 71.073
T [K]	296(2)	296(2)
μ [mm^{-1}]	1.089	0.608
scan method	ω-2θ	ω
2θ (max) [°]	48	48
total no. of reflections	9527	7381
no. of unique reflections	8952	6950
no. of observed reflections	6726	4386
data-to-parameter ratio	17.32	19.03
R [$I > 2\sigma(I)$]	0.076	0.063
$wR2$ (all data)	0.207	0.186

tions, and all other atoms were refined anisotropically. The benzene molecules of **8** · 2 C_6H_6 are disordered and were refined on two positions with an occupancy factor of 0.5 for each. One of the 2,4,6-*i*$Pr_3C_6H_2$ and the 2,6-$Me_2C_6H_3$ groups, respectively, of **17** are disordered and were refined on two positions with occupancy factors of 0.5. Crystal data and numerical data of the structure determinations are given in Table 1[19].

☆ Dedicated to Professor *Hans Bürger* on the occasion of his 60th birthday.

[1] M. Weidenbruch, A. Stilter, K. Peters, H. G. von Schnering, *Chem. Ber.* **1996**, *123*, 1565−1567.

[2] Reviews: M. Driess, H. Grützmacher, *Angew. Chem.* **1969**, *108*, 900−929; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 827−856; K. M. Baines, W. G. Stibbs, in *Multiply Bonded Main Group Metals and Metalloids* (Eds.: R. West, F. G. A. Stone), Academic Press, San Diego, U.S.A., **1996**, p. 275−324.

[3] D. E. Goldberg, P. B. Hitchcock, M. F. Lappert, K. M. Thomas, T. Fjeldberg, A. Haaland, B. E. R. Schilling, *J. Chem. Soc., Dalton Trans.* **1986**, 2387−2394.

[4] G. Trinquier, J. P. Malrieu, *J. Am. Chem. Soc.* **1987**, *109*, 5303−5315; G. Trinquier, *ibid.* **1990**, *112*, 2130−2137.

[5] R. S. Grev, H. F. Schaefer III, K. M. Baines, *J. Am. Chem. Soc.* **1990**, *112*, 9458−9467.

[6] T. L. Windus, M. S. Gordon, *J. Am. Chem. Soc.* **1992**, *114*, 9559−9568.

[7] H. Jacobsen, T. Ziegler, *J. Am. Chem. Soc.* **1994**, *116*, 3667−3679, and references cited therein.

[8] J. T. Snow, S. Murakami, S. Masamune, J. D. Williams, *Tetrahedron Lett.* **1984**, *38*, 4191−4194.

[9] P. B. Hitchcock, M. F. Lappert, S. J. Miles, A. J. Thorne, *J. Chem. Soc., Chem. Commun.* **1984**, 480−482.

[10] S. A. Batcheller, T. Tsumuraya, O. Tempkin, W. M. Davis, S. Masamune, *J. Am. Chem. Soc.* **1990**, *112*, 9394−9395.

[11] M. Kira, T. Iwamoto, T. Maruyama, C. Kabuto, H. Sakurai, *Organometallics* **1996**, *15*, 3767−3769.

[12] M. Weidenbruch, H. Kilian, K. Peters, H. G. von Schnering, H. Marsmann, *Chem. Ber.* **1995**, *128*, 983−985.

[13] P. Jutzi, H. Schmidt, B. Neumann, H.-G. Stammler, *Organometallics* **1996**, *15*, 741−746.

[14] [14a] M. Weidenbruch, A. Schäfer, K. L. Thom, *Z. Naturforsch., B* **1983**, *38*, 1695−1996. − [14b] M. Weidenbruch, A. Lesch, K. Peters, *J. Organomet. Chem.* **1991**, *407*, 31−40.

[15] S. Masamune, L. R. Sita, *J. Am. Chem. Soc.* **1985**, *107*, 6390−6391.

[16] A. Schäfer, M. Weidenbruch, W. Saak, S. Pohl, H. Marsmann, *Angew. Chem.* **1991**, *103*, 873−874 and 978−979; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 834−836 and 962−964.

[17] M. Weidenbruch, A. Schäfer, H. Kilian, S. Pohl, W. Saak, H. Marsmann, *Chem. Ber.* **1992**, *125*, 563−566.

[18] G. M. Sheldrick, SHELXL 93, Universität Göttingen, Germany, **1993**.

[19] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100094. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax: int. code + (1223) 336-033. e-mail: deposit@chemcrys.cam.ac.uk].

[20] H. G. von Schnering, K. Peters, Stuttgart, personal communication.

[96273]