Sulfur Compounds, Part 186[◇]

The Synthesis of Cyclic Organosulfur Compounds from $(C_5H_5)_4Ti_2C_2S_4$ by Ligand Transfer Reactions[1]

Ralf Steudel*, Ursula Westphal, and Joachim Pickardt

Institut für Anorganische und Analytische Chemie, Sekr. C2, Technische Universität Berlin,
D-10623 Berlin, Germany
Telefax: (internat.) +49(0)30-31426519
E-mail: steudel@wap0204.chem.tu-berlin.de

Received February 8, 1995

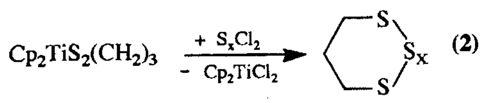
Key Words: Titanocene complexes / Organosulfur ligands / Ligand transfer / Organosulfur heterocycles / Sulfur-sulfur bonds

The tetrathiaoxalate complex $Cp_4Ti_2C_2S_4$ (**1**) reacts with an equimolar amount of $COCl_2$ to give the blue-green mononuclear complex $Cp_2TiC_2S_4CO$ (**4**). This reaction is analogous to the known reactions of **1** with SCl_2 or S_2Cl_2. However, when **1** was treated with equimolar amounts of the bifunctional sulfenyl chlorides 1,2-$C_2H_4(SCl)_2$ (**5**), 1,3-$C_3H_6(SCl)_2$ (**6**) or 1,2-$C_6H_4(SCl)_2$ (**7**), the bi- or monocyclic tetrakisdisulfanes $C_6H_8S_8$ (**9b**), $C_8H_{12}S_8$ (**10**), and $C_{14}H_8S_8$ (**11**), respectively, were obtained. The X-ray crystal structure analysis of **11** · CS_2 showed that **11** possesses C_i symmetry with a central exocyclic CC double bond similar to tetrathiafulvalenes: $C_6H_4(\mu\text{-}S_2)_2C{=}C(\mu\text{-}S_2)_2C_6H_4$.

Titanocene complexes with sulfur-containing ligands are very useful reagents in the synthesis of novel homocyclic or heterocyclic sulfur compounds, both inorganic and organic[2]. In this way a large number of interesting sulfur-rich species were prepared for which there is hardly any other synthetic route available. For example, dichlorosulfanes S_xCl_2 react with Cp_2TiS_5 and $Cp_2TiS_2(CH_2)_3$ to afford sulfur homocycles[3] and methylenepolysulfanes[4], respectively; eq. (1) and (2).

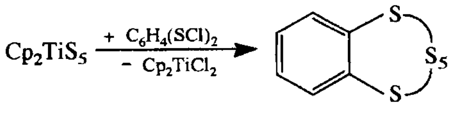
$$Cp_2TiS_5 \xrightarrow[-\ Cp_2TiCl_2]{+\ S_xCl_2} S_{5+x} \qquad (1)$$

$$(Cp = \eta^5\text{-}C_5H_5)$$

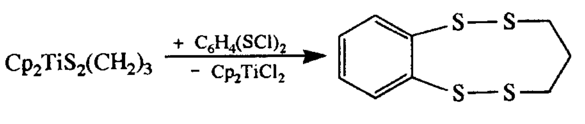


(2)

The use of bifunctional sulfenyl chlorides also afforded cyclic polysulfanes[5]; eq. (3) and (4).

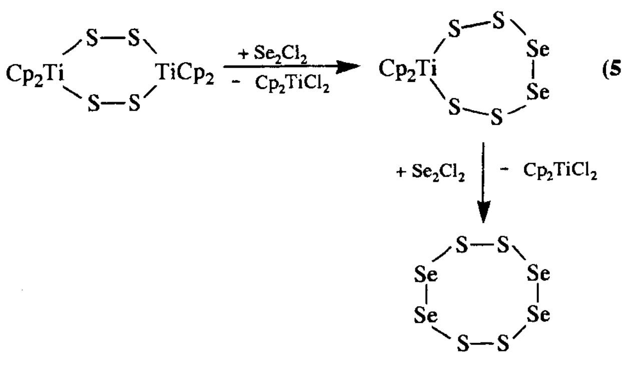


(3)



(4)

In recent years a number of dinuclear titanocene complexes were synthesized in which sulfur containing ligands are bridging the two titanium centers. Examples are $Cp_2Ti(\mu\text{-}S_2)_2TiCp_2$[6] and $Cp_2Ti(\mu\text{-}S_3)_2TiCp_2$[7]; both complexes react with lower dichlorosulfanes (SCl_2, S_2Cl_2) and with dichlorodiselane Se_2Cl_2 first by removal of one Cp_2Ti unit followed by formation of the corresponding metal-free cyclic compound and titanocene dichloride; eq. (5)[8].



(5)

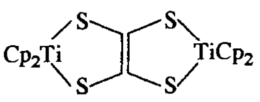
However, it must be stressed that the intermediate mononuclear complex was not always been observed in these reactions. In the present work we show that the mechanism of such reactions of dinuclear titanocene complexes with SCl compounds depends on the chain length of the latter. For this study we selected the tetrathiolato complex $Cp_4Ti_4C_2S_4$ (**1**) which was obtained by reaction of $Cp_2Ti(CO)_2$ with CS_2 and forms stable, soluble crystals the structural analysis of which has shown that the bridging

---

[◇] Part 185: K. Bergemann, M. Kustos, P. Krüger, R. Steudel, *Angew. Chem.*, in print.

0009–2940/95/0606–0561 $ 10.00+.25/0

ligand is planar while the titanium centers are located above and below this plane, respectively[9]:

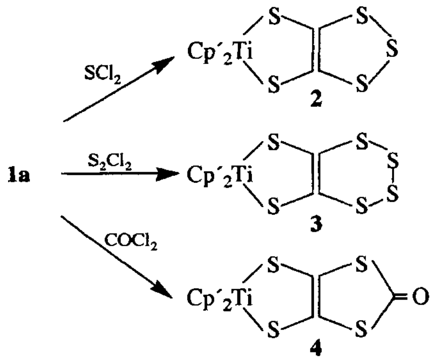


1

Because of its better solubility we have also used the methylated derivative $Cp'_4Ti_2C_2S_4$[10] (**1a**; Cp' = $CH_3C_5H_4$) in the present work. Both compounds react practically in an identical manner.

Results and Discussion

Previously we have shown that **1** and **1a** react with SCl_2 and S_2Cl_2, respectively, to give the mononuclear chelate complexes **2** and **3**[10]; eq. (6) and (7).



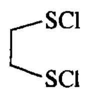
(6)

(7)

(8)

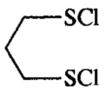
Phosgene reacts analogously with **1a** to give the carbonyl **4**; eq. (8). Like **2** and **3**, **4** forms air-stable, blue-green crystals which are light-sensitive and soluble in chlorinated hydrocarbons. The solutions exhibit an absorption maximum near 640 nm responsible for the color. The EI-mass spectrum of **4** shows a signal for the molecular ion; the ^{1}H-NMR spectrum is characterized by broad lines in the Cp region due to conformational motions of the five-membered TiS_2C_2 rings.

The reactions according to eqs. (6)–(8) must proceed in several steps. In the first step a chlorine atom attacks one of the titanium atoms forming a Ti–Cl bond and simultaneously an E–S bond (E = S, C). Model studies[11] show that in these particular reactions the second chlorine atom of the reagents used can only attack the *same* titanium center resulting in the formation of Cp'_2TiCl_2 since the distance to the *second* titanium atom is too large. Therefore, the first isolable products are two mononuclear complexes. However, when the chain length of the reagent and therefore the distance between the two chlorine atoms is increased there is a chance that after the first Ti–Cl bond has been formed the second chlorine atom could attack the *other* titanium atom. To check this possibility the bifunctional sulfenyl chlorides **5**–**7** were treated with **1** or **1a**:



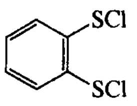
$C_2H_4(SCl)_2$

5



$C_3H_6(SCl)_2$

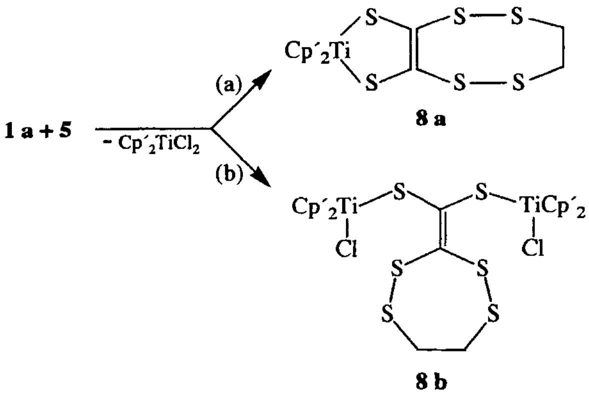
6



$C_6H_4(SCl)_2$

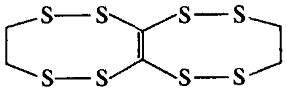
7

In the case of 1,2-$C_2H_4(SCl)_2$ the two pathways discussed would result in the initial formation of the complexes **8a** or **8b**; eq. (9).

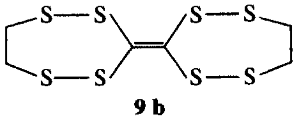


(9)

The following reaction with a second equivalent of 1,2-$C_2H_4(SCl)_2$ would furnish the products **9a** or **9b**:



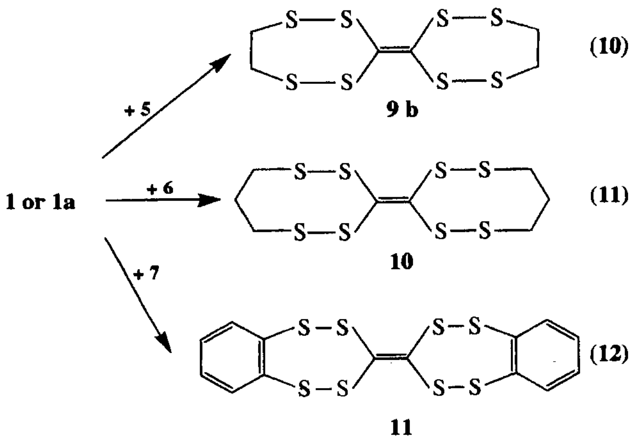
9a



9b

The reaction of **1a** with **5** yielding **9** has already been studied[12], and on the basis of analogous reactions like (6) and (7) it was thought that complex **8a** would be the intermediate and that the product $C_6H_8S_8$ would possess structure **9a**. The recorded spectra (MS, ^{1}H NMR, UV) did not allow a differentiation to be made between the isomeric structures **9a** and **9b** which we discussed already in our previous publication[12].

Therefore, two additional bis(sulfenyl chlorides), **6** and **7**, were allowed to react with **1** or **1a**. The product obtained from sulfenyl chloride **7** yielded crystals suitable for an X-ray structural analysis which revealed that the molecule has a structure with an *exocyclic* CC double bond (Fig. 1). On the basis of this result we believe that all three bis(sulfenyl chlorides) (**5**–**7**) react with **1** or **1a** accordingly; eq. (10)–(12). In other words, the substance formerly described as **9a**[12] is in fact [3,3']Bi[1,2,4,5-tetrathiepanylidene] **9b**. Reactions (11) and (12) take place at 15 °C; **10** was obtained as a pale-yellow powder in 52% yield while orange-yellow crystals of **11** were isolated in 75% yield.

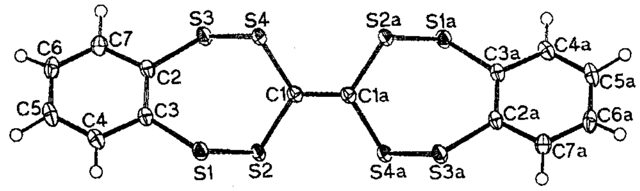


In the solid state **10** and **11** are air-stable but light-sensitive. In solution (CS_2, CH_2Cl_2) **10** slowly decomposes to S_8 and a sulfur-containing polymer. The bicyclic, tricyclic, and tetracyclic tetrakisdisulfane **11** is more stable than **10** in solution (CS_2, toluene, CH_2Cl_2). Compound **11** decomposes at 210°C but nevertheless the EI-mass spectrum shows a signal for the molecular ion. In contrast, the EI-MS of **10** exhibits fragments only, the heaviest at m/z = 206 ($M^+ - C_2H_6S_4$).

From CS_2 solution, **11** crystallizes as triclinic solvate $C_{14}H_8S_8 \cdot CS_2$. In order to prevent loss of solvent during the X-ray irradiation the single crystal was cooled to 170 K. The molecules of **11** exhibit perfect C_i symmetry. To a first approximation all atoms of **11** except the sulfur atoms (and with the exception of the CS_2 molecule) are located in a plane. The central C_2S_4 group is planar and the two C_6H_4 units are coplanar; the angle between these two planes (C_2S_4/C_6H_4) amounts to 47.5(9)°. The two seven-membered rings are twisted; the signs of the torsional angles within these rings are + − + − − + −. At the two independent SS bonds, the torsional angles are 93.2(1) and 92.7(1)°, i.e. close to the ideal value of 90°. Therefore, the SS bond lengths (204.0 and 204.4 pm) are close to the single bond value of 205 pm[13]. All six CS bond lengths are in the range 176.0−177.6 pm. Remarkably, the torsional angle S1−C3−C2−S3 (11.1°) is quite different from the ideal value of zero expected under unstrained conditions. The central CC bond (135.2 pm) is shorter than in $Cp_4Ti_2C_2S_4$ (141 pm[9]) but almost identical to the values of 134−138 pm observed in tetrathiafulvalene derivatives[14].

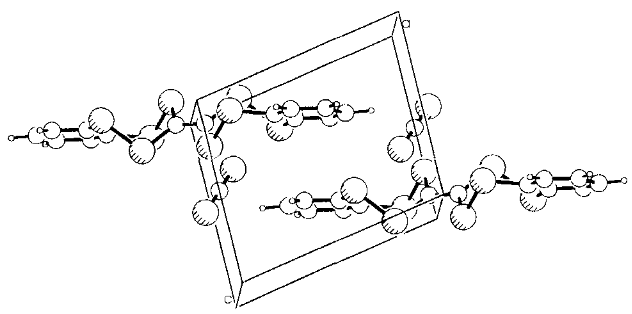
In the crystal the molecules of **11** are stapled in such a way that benzene rings of neighboring molecules are located almost exactly on top of each other (Figure 2). The CS_2 molecules fill "holes" of the crystal lattice and have no shorter than van der Waals contacts to the molecules of **11**.

Figure 1. Molecular structure of **11**



Selected bond lengths [pm], angles [°] and torsisonal angles [°]: S1−S2 204.4(1), S1−C3 177.3(2), S2−C1 177.0(3), S3−S4 204.0(1), S3−C2 177.6(3), S4−C1 176.0(2), C1−C1a 135.2(3), S2−S1−C3 106.9(1), S1−S2−C1 101.6(1), S4−S3−C2 107.0(1), S3−S4−C1 100.8(1), S2−C1−S4 117.9(2), S2−C1−C1a 120.5(2), S4−C1−C1a 121.6(2), S3−C2−C3 127.6(2), S1−C3−C2 126.7(2), S1−C3−C4 113.9(2), C3−S1−S2−C1 92.7(1), S2−S1−C3−C2 −45.4(2), S2−S1−C3−C4 139.9(2), S1−S2−C1−S4 −42.4(2), S1−S2−C1−C1a 139.0(2), C2−S3−S4−C1 93.2(1), S4−S3−C2−C3 −44.3(2), S3−S4−C1−S2 −45.6(2), S3−S4−C1−C1a 133.0(2), S2−C1−C1a−S2a 180.0(8), S3−C2−C3−S1 11.1(3).

Figure 2. Unit cell of **11** · CS_2 showing the stacking of the benzene rings of neighboring molecules as well as the position of the solvent molecule



Experimental[11]

Methods: HPLC analyses with liquid-chromatograph Varian 5000 (computer-controlled) equipped with Valco loop injector (10 µl), UV detector (GAT LCD 501; 254 nm) and Hewlett-Packard integrator (3390 A). Column: Waters Radial-Pak (l = 10 cm, *i. d.* = 8 mm; octadecylsilane, particle size 10 µm); eluent: methanol (distilled from $MgSO_4$). − UV: Waters diode array detector 990 (512 diodes; 190−800 nm; connected to the HPLC apparatus) with NEC data processing system: relative extinctions are given (strongest signal = 100). − ^1H-NMR: Bruker WP80 (internal standard TMS). − MS: Varian MAT 311A (EI, 70 eV). − Melting points: Büchi 510. − CH-Analysis: Perkin-Elmer 2400.

Procedures: All preparations were carried out with exclusion of light and moisture. Solvents were carefully dried (CH_2Cl_2, CCl_4, CS_2, distilled from P_4O_{10}, toluene from $CaCl_2$, THF from KOH and Na). $COCl_2$ (Merck; 20% in toluene) was used as received. **5** and **7** were prepared from the dithiols by chlorination with Cl_2 or SO_2Cl_2, and **6** was obtained by cleavage of the SS bond of 1,2-dithiolane by Cl_2[15].

Carbonyl Complex (**4**): To a solution of 72 mg of **1a** (0.13 mmol), dissolved in 30 ml CCl_4, was added dropwise at 0°C with stirring and exclusion of light a solution of 25 mg of $COCl_2$ (0.25 mmol) in toluene (see above) diluted with 5 ml of CCl_4. During stirring for 16 h the temperature was allowed to rise to 20°C resulting in evaporation of excess $COCl_2$ and color change of the mixture from violet to blue-green. Rapid filtration of the solution through a short column (l = 4 cm, *i. d.* = 25 mm, silica gel 60) at 15°C resulted in adsorption of **4** and $Cp_2^*TiCl_2$. Compound **4** was extracted with THF, the volume of the extract reduced to 5 ml by evaporation of the solvent in vacuo and the residual solution cooled to −26°C for 20 h, resulting in blue-green crystals of **4** (14 mg; 28%); storage at

4 °C. – IR ($CS_2/CDCl_3$ solution): $\tilde{\nu}$ = 1680 cm^{-1} (C=O). – ^1H-NMR ($CDCl_3$; 25 °C): δ = 5.85 (d, br., 4 H), 5.51 (s, br., 4 H), 2.18 (s, 3 H), 1.80 (s, 3 H). – MS (EI, 70 eV, T_p = 160 °C), *m/z* (%): 386 (42) [M^+], 307 (12) [$M^+ - CH_3C_5H_4$], 247 (20), 206 (53), 126 (22), 77 (44), 28 (74). – UV (methanol): λ_{max} (rel. int.) = 240 (100), 288 (33), 284 (6), 634 (10) nm. – $C_{15}H_{14}OS_4Ti$ (386.4): calcd. C 46.63, H 3.65; found C 45.78, H 3.54.

[3,3']Bi[1,2,4,5-tetrathiocanylidene] (**10**): To a solution of 150 mg of **1a** (0.266 mmol) in 150 ml of CH_2Cl_2, was added dropwise within 30 min at 15 °C, a solution of 94 mg of **6** (0.53 mmol) in 5 ml of CCl_4. During the addition the color of the mixture changed from dark violet to orange-red. On cooling to −78 °C for 18 h, a pale-yellow product precipitated which was isolated and extracted with CS_2 (100 ml) at 20 °C. Evaporation of CS_2 from the extract yielded light yellow **10** (50 mg; 52%); m.p. 176 °C (dec). – ^1H-NMR (CS_2/C_6D_6): δ = 3.20 (m, br.), 2.65 (m, br.). – MS (EI, 70 eV, T_p = 240 °C): *m/z* (%) = 206 (12), 134 (100), 76 (42). – UV (methanol): λ_{max} = 214, 338 nm. – $C_8H_{12}S_8$ (364.7): calcd. C 26.35, H 3.32; found 25.43, H 3.01. The light-sensitivity of **10** prevented the measurement of reliable IR and Raman spectra.

[7,7']Bi[5,6,8,9-tetrathia-benzocycloheptenylidene] (**11**): To a solution of 250 mg of **1** (0.492 mmol) in 200 ml of CH_2Cl_2 was added dropwise within 1 h at 15 °C a solution of 208 mg of **7** (0.984 mmol) in 20 ml of CH_2Cl_2. The color of the mixture changed from violet to red-orange. The completion of reaction (11) was checked by HPLC. Reduction of the volume in vacuo to 10 ml and cooling to −78 °C for 12 h afforded a red precipitate (**11** + Cp_2TiCl_2) which was isolated and extracted with CH_2Cl_2 till the extracts were no longer red. The residue was dissolved in CS_2 (50 ml) and after filtration of the solution 10 ml of toluene were carefully laid on top of the CS_2 phase. Cooling to −78 °C for 12 h resulted in 160 mg (75%) of **11**: m.p. 210 °C (dec.). – Raman (solid): $\tilde{\nu}$ = 1470 (C=C), 524 (SS) cm^{-1}. – IR (KBr): $\tilde{\nu}$ = 1505 (s), 1445 (m), 1418 (m), 1250 (m), 745 (s), 730 (m), 460 (m), 390 (m), 375 (m) cm^{-1}. – ^1H-NMR (CS_2/[D_8]THF): δ = 6.95–7.01 (4 H), 7.04–7.09 (4 H). – MS (EI, 70 eV, T_p = 250 °C): *m/z* (%) = 432 (0.5) [M^+], 400 (0.3) [$M^+ - S$], 368 (0.6) [$M^+ - S_2$], 336 (1) [$M^+ - S_3$], 304 (15) [$M^+ - S_4$], 228 (4) [$M^+ - C_6H_4S_4$], 196 (6) [$M^+ - C_6H_4S_5$], 72 (100) [$C_6H_4S_3^+$]. – $C_{14}H_8S_8$ (432.7): calcd. C 38.86, H 1.86, S 59.27; found C 39.18, H 2.19, S 58.25. – UV (methanol): λ_{max} = 254, 284 nm.

Crystal Structure Analysis of 11 · CS_2[16]: Single crystals of **11** · CS_2 were obtained as described above and measured at 170 K; crystal size: 0.3 × 0.4 × 0.5 mm; triclinic, space group $P\bar{1}$; Z = 1; a = 758.1(6), b = 790.0(1), c = 870.4(4) pm, α = 92.49(3), β = 97.95(5), γ = 107.81(4)°; V = 489.5(5) · 10^{-30} m^3; $\rho_{calcd.}$ = 1.726 g cm^{-3}; μ(Mo-K_α) = 1.08 mm^{-1}; M = 508.9. – 2174 unique reflections were measured and 2069 with $F > 4\sigma(F)$ were used in the refinement to R = 0.046; R_w = 0.051. No absorption corrections were made. The structure was solved by direct methods[17] and refined with anisotropic thermal parameters for the non-hydrogen atoms, H atoms refined isotropically, atomic scattering factors were taken as supplied by SHELX[18]; geometrical calculations and plots were done with PLUTON[19].

---

[1] Presented in parts at the "16th International Symposium on the Organic Chemistry of Sulfur" (Merseburg, July 10–15, **1994**) and at the "7th International Symposium on Inorganic Ring Systems" (Banff, August 7–12, **1994**).

[2] Review: R. Steudel, in *The Chemistry of Inorganic Ring Systems* (Ed.: R. Steudel), Elsevier, Amsterdam **1992**, p. 233.

[3] Reviews: M. Schmidt, *Angew. Chem.* **1973**, *85*, 474; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 445; R. Steudel, *Top. Curr. Chem.* **1982**, *102*, 149.

[4] U. Westphal, R. Steudel, *Phosphorus Sulfur Silicon* **1992**, *65*, 151.

[5] R. Steudel, M. Kustos, *Phosphorus Sulfur Silicon* **1991**, *62*, 127; R. Steudel, S. Förster, J. Albertsen, *Chem. Ber.* **1991**, *124*, 2357.

[6] D. M. Giolando, T. B. Rauchfuss, A. L. Rheingold, S. R. Wilson, *Organometallics* **1987**, *6*, 667.

[7] C. M. Bolinger, T. B. Rauchfuss, S. R. Wilson, *J. Am. Chem. Soc.* **1981**, *103*, 5620.

[8] R. Steudel, D. Jensen, M. Papavassiliou, *Phosphorus Sulfur Silicon* **1989**, *41*, 349.

[9] H. A. Harris, A. D. Rae, L. F. Dahl, *J. Am. Chem. Soc.* **1987**, *109*, 4739.

[10] R. Steudel, U. Westphal, *J. Organomet. Chem.* **1990**, *388*, 89.

[11] U. Westphal, *Doctoral Dissertation*, Techn. Univ. Berlin, **1994**.

[12] U. Westphal, R. Steudel, *Chem. Ber.* **1991**, *124*, 2141.

[13] R. Steudel, *Angew. Chem.* **1975**, *87*, 683; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 655.

[14] K. Swaminathan, P. J. Carroll, J. D. Singh, H. B. Singh, *Acta Crystallogr. Sect. C* **1994**, *50*, 1958; S. Hebrard, G. Bravic, J. Gaultier, D. Chasseau, *Acta Crystallogr. Sect. C* **1994**, *50*, 1892.

[15] R. Schubart, *Methoden Org. Chem.* (Houben-Weyl), 4th ed. **1985**, *vol. E 11*, p. 72, 76.

[16] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-401474, the name of the authors and the journal citation.

[17] G. M. Sheldrick, *SHELXS-86, Program for Crystal Structure Solution*, Univ. Göttingen **1986**.

[18] G. M. Sheldrick, *SHELXS-76, Program for Crystal Structure Determinations*, Univ. of Cambridge **1976**.

[19] A. L. Spek, The Euclid Package, in: *Computational Crystallography* (Ed.: D. Sayre), Clarendon Press, Oxford **1982**, p. 528.

[95017]