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Journal of Organometallic Chemistry 579 (1999) 18–23

Journal of Organo metallic Chemistry

A methylene bridged dialuminium compound as a chelating Lewis acid—complexation of azide and acetate anions by $R_2Al-CH_2-AlR_2$ $[R = CH(SiMe_3)_2]$

Werner Uhl *, Frank Hannemann

Fachbereich Chemie der Universität, Postfach 2503, D-26111 Oldenburg, Germany

Received 22 October 1998

Abstract

Suspensions of sodium azide or sodium acetate in diethyl ether were treated with the methylene bridged dialuminium compound $R_2Al-CH_2-AlR_2$ $[R = CH(SiMe_3)_2]$ **1**, which has two coordinatively unsaturated aluminium atoms, and the crown ether [18]crown-6 for the coordination of the sodium ions. In both cases, compound **1** reacted as a chelating Lewis acid, and the salts readily dissolved at room temperature. As shown by crystal structure determinations of the products **7** (azide) and **8** (acetate), six-membered heterocycles were formed by the coordination of both aluminium atoms to the terminal nitrogen atoms of the linear azido group or both oxygen atoms of the acetato group. Each product crystallized with the cation $[Na([18]crown-6)(iPr_2O)]^+$.

Keywords: Aluminium; Chelates; Lewis acids

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1. Introduction

Chelating Lewis acids are important substances for the complexation and recognition of anions, but by far the most of these ligands were obtained up to now by the protonation of amino groups of macrocyclic or polycyclic compounds [1]. However, similar properties are to be expected also for polynuclear organoelement compounds with coordinatively unsaturated atoms of the elements of the third or fourth main-group, and indeed the synthesis of such Lewis acids is of particular interest in current chemical research [2–5]. A corresponding compound was isolated and completely characterized recently in our group, which was the first stable methylene bridged tetra-alkyl dialuminium derivative known in the literature (**1**, Scheme 1) [2]. **1** has four bulky substituents to prevent a dismutation reaction and possesses two coordinatively unsaturated aluminium atoms. However, by far the most of these potentially useful chelating Lewis acids were up to now not investigated concerning their ability to actually act as a chelating ligand. Exceptions are, for instance, an aromatic diboron compound with a single example of a hydrido bridge [3], methylene bridged polytin compounds coordinating fluoride ions [4] and the dialuminium derivative **1** [2], of which some chelate complexes were isolated and characterized [6–11]. Usually, these complexes gave heterocycles by the coordination of both aluminium atoms to, for instance, one hydride (**2**) [6], hydroxide [7], or thiomethanolate anion [8]. The reaction of **1** with $LiCH(PMe_2)_2$ resulted in the formation of a remarkable five-membered ring (**3**), in which one Al atom was coordinated to the central carbanion and the other one to a phosphorus atom [9]. A terminal coordination of a neopentyl group was observed by the treatment of **1** with neopentyllithium (**4**) [10]. The complexes obtained by the reaction of **1** with multifunctional inorganic anions like nitrate (**5**) or nitrite (**6**) are, however, much more important concern-

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* Corresponding author. Tel. +49-441-798-36-60; fax: +49-441-798-33-52.

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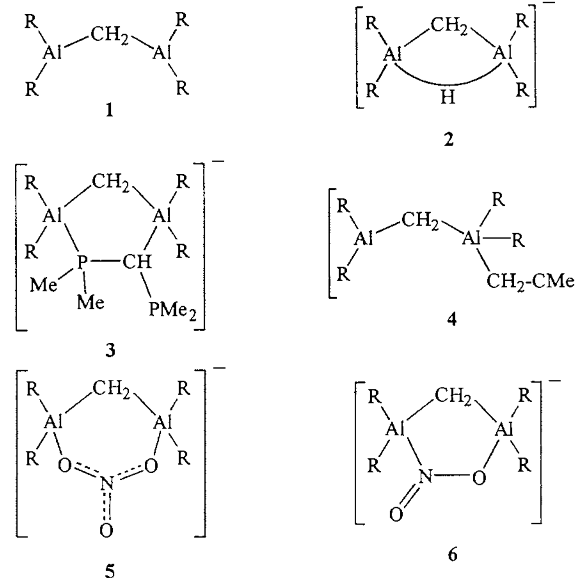
PII: S0022-328X(98)01150-4

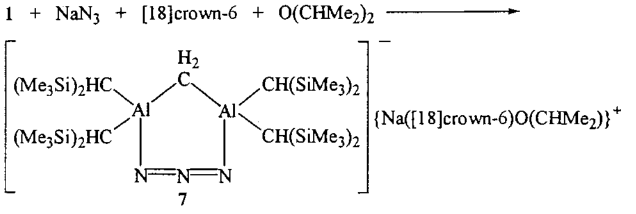


Scheme 1. [R = $CH(SiMe_3)_2$].

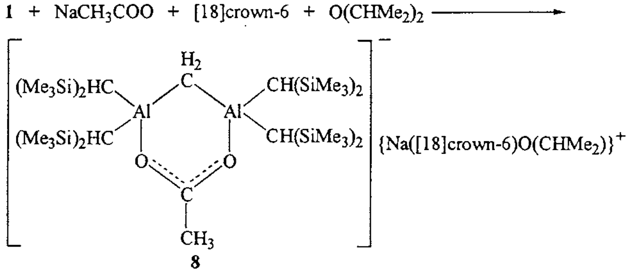
ing the application of these chelating Lewis acids as anion receptors, and both salts, sodium nitrite and lithium nitrate, became readily soluble in THF upon addition of equivalent quantities of **1** [11]. We wish to report here on the reactions of **1** with sodium azide, sodium acetate and some other ionic compounds, which should give better insight into the reactivity of **1**, its capability to give stable chelate complexes with anions and its usefulness in phase transfer processes.

2. Reactions of the methylene bridged dialuminium compound 1 with NaN_3 and $NaCH_3COO$

Sodium azide is insoluble even in a large excess of THF. But after addition of one equivalent of the chelating Lewis acid μ-methylene tetraalkyldialuminium $R_2Al-CH_2-AlR_2$ **1**, the complete dissolution of the crystalline salt occurred within several hours by stirring at room temperature. Reaction control by NMR spectroscopy showed that **1** was completely consumed and a new methylene bridged compound with tetracoordinated aluminium atoms was formed. However, this product could not be isolated and purified by recrystallization, because it decomposed slowly by reconversion of the starting compounds upon concentration of its solutions. Thus, the behavior of the azido complex is quite different from that of the nitrato (**5**) or nitrito (**6**) compounds cited above [11], which were isolated in a stable form with the $[Li(THF)_4]^+$ and $[Na(THF)_3]^+$ counterions. A stable product (**7**) of the reaction of **1** with sodium azide was obtained finally by the addition of the crown ether [18]crown-6 to a reaction mixture in diethyl ether as a solvent (Eq. (1)). **7** was isolated in a pure form after recrystallization from diisopropyl ether in a moderate yield of 54% and contained the cation $\{Na([18]crown\text{-}6)[O(iPr)_2]\}^+$. Similar conditions by using the chelating crown ether were required for the synthesis of a stable sodium acetate adduct of **1** (**8**, Eq. (2)). Both crystalline compounds became amorphous in vacuo (**7**) or at normal pressure after removal of the solvent even at low temperature (**8**), which in all cases is accompanied by a decreasing content of diisopropyl ether. The crystals have melting points of 162 and 180°C (**7** and **8**, respectively). In contrast, we observed no reaction under similar conditions, when we treated suspensions of sodium chlorite, sodium sulfate or lithium carbonate with **1** in diethyl ether or THF solution.



(1)



(2)

Similar to the chelate complexes cited above, the ^1H- and ^{13}C-NMR spectroscopic characterization of the products **7** and **8** yielded some important changes in comparison to the neutral starting compound **1**, and all resonances of groups directly bound to the aluminium atoms showed a significant shift to high field. The protons of the $Al-CH_2-Al$ group of **1** appeared at δ −0.50 ppm, and we observed the methine protons at δ −0.22 ppm and the corresponding carbon atoms at δ 13.2 ppm. In **7** and **8**, these resonances were shifted to $\delta(AlCH_2Al) = -1.52$ and -1.45 ppm, $\delta(AlCHSi_2) = -1.05$ and -1.16 ppm, $\delta(AlCHSi_2) = 5.0$ and 3.6 ppm, respectively. Such shifts to a higher field are very indicative of the enhancement of the coordination number at the aluminium atoms from three to four [6–12]. The most important absorptions in the IR spectra are observed at 2112 cm^{-1} of the N–N stretching vibration in compound **7** and at 1582 cm^{-1} of the CO_2 group with a delocalized π bond for **8**. Both absorptions are in the characteristic ranges usually observed for azido or acetato ligands [13,14].

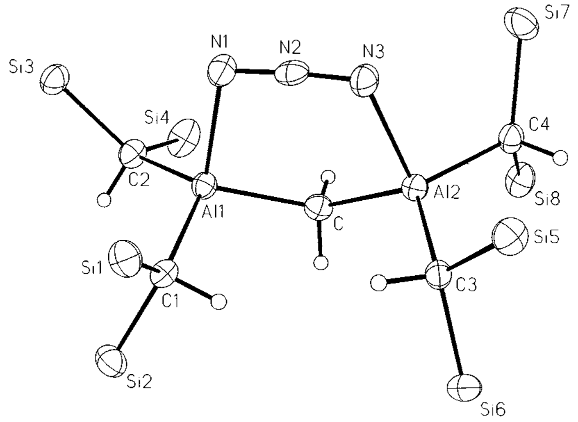


Fig. 1. Molecular structure and numbering scheme of the anion of **7**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity. Selected bond lengths (pm) and angles (°): Al1–C 197.4(3), Al2–C 197.1(3), Al1–C1 202.1(3), Al1–C2 201.1(3), Al2–C3 202.6(3), Al2–C4 201.7(3), Al1–N1 205.8(3), Al2–N3 208.9(3), N1–N2 118.4(3), N2–N3 117.8(3), Al1–C–Al2 123.2(2), C–Al1–N1 96.8(1), Al1–N1–N2 105.5(2), N1–N2–N3 175.6(3), N2–N3–Al2 108.8(2), N3–Al2–C 96.8(1).

3. Crystal structures of 7 and 8

The molecular structures of the azido complex **7** and the acetato complex **8** are depicted in Figs. 1 and 2. In both compounds, six-membered heterocycles are formed by the coordination of each aluminium atom of **1** to one of the terminal nitrogen or oxygen atoms of the azido or acetato ligand. Nevertheless, the shapes of the heterocycles are quite different and contain an almost linear azido group with an angle N1–N2–N3 of 175.6° in compound **7** and a trigonal planar acetato group with the sum of the angles at C(a) of 360.0° in compound **8**. Both heterocycles adopt an envelope conformation, and both aluminium atoms and all three atoms of the chelating anion lie almost ideally within a plane and the largest deviation from that plane is observed for the atom N1 with 12.6 pm in compound **7** and for the atom O1 with 10.6 pm in compound **8**. The carbon atoms of the methylene bridges between both aluminium atoms deviate from this planes by 57.1 pm in **7** and 67.7 pm in **8**.

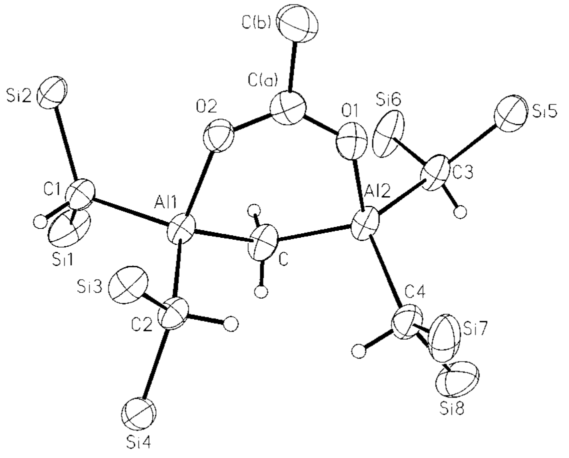


Fig. 2. Molecular structure and numbering scheme of the anion of **8**; the thermal ellipsoids are drawn at the 40% probability level; methyl groups are omitted for clarity. Selected bond lengths (pm) and angles (°): Al1–C 195.9(4), Al1–O2 189.2(3), Al1–C1 202.5(4), Al1–C2 204.0(3), Al2–C 196.0(4), Al2–O1 188.9(3), Al2–C3 202.9(4), Al2–C4 202.5(4), C(a)–O1 126.3(5), C(a)–O2 124.9(5), Al1-C-Al2 113.4(2), C–Al1–O2 99.1(2), Al1–O2–C(a) 133.0(2), O2–C(a)–O1 126.2(3), C(a)–O1–Al2 131.3(3), O1–Al2–C 102.2(2).

The methylene bridged tetraalkyldialuminium moieties of both compounds are quite similar. The Al–C distances to the $CH(SiMe_3)_2$ substituents are 201.9 (**7**) and 203.0 pm (**8**) on average. Similar to the dialuminium complexes discussed above [6–11], they are elongated compared with the Al–C bond lengths to the carbon atoms of the methylene bridges [197.3 (**7**) and 196.0 pm (**8**)], which may be caused by the accumulation of negative charge at the bridging atoms and an enlargement of the electrostatic contribution to the Al–C bond strength. As expected from the enhancement of the coordination number at the aluminium atoms [6–12], all distances are lengthened compared with the starting compound **1** [2], which had the corresponding values at 195.7 and 193.8 pm. The structure of **1** showed a strongly enlarged Al–C–Al angle of 129.6° caused by a steric and electrostatic repulsion between the bulky substituents and the positively charged Al atoms [2]. Owing to the formation of a six-membered heterocycle with an almost regular geometry this angle is reduced in compound **8** to 113.4° similar to the derivatives cited above. But as a consequence of the coordination of the aluminium atoms to the linear azido group in compound **7**, a larger separation of the metal atoms results, and the Al–C–Al angle is enlarged to 123.2°, which is more similar to that of the starting compound **1**.

The azido group in **7** shows an unusual 1,3-coordination by two aluminium atoms, and due to the formation of the heterocycle acute angles Al–N–N of 105.5 and 108.8° result. A similar, but almost linear 1,3-coordination was observed for the trimer of the highly sterically shielded dialkylaluminium azide $[(Me_3Si)_2CH]_2AlN_3$, which owing to a steric and electrostatic repulsion between the dialkylaluminium groups gave a 12-membered heterocycle in the solid state [14]. In most cases, however, the geminal coordination of one of the terminal nitrogen atoms of the azido groups by two aluminium or gallium atoms is detected by IR spectroscopy or crystal structure analysis [15]. The geminal coordination of the terminal nitrogen atom is also observed in the related nitrile imide derivatives of aluminium or gallium [16]. The unusual structure of compound **7** may be caused by the electrostatic repulsion between the positively charged aluminium atoms, the steric interaction between the bulky substituents and the steric strain, which has to be expected in a four-membered Al_2CN heterocycle with an exocyclic N_2 group. Four-membered heterocycles derived from **1** have, however, been obtained before with bridging monodentate ligands like hydrido, hydroxo or thiomethanolato anions as described above (see Introduction) [6–8]. As expected, the N–N bond lengths are quite similar (118.1 pm on average) and correspond well to the standard value of 118 pm [17] observed for ionic azides, but they are lengthened compared to the distances observed for the trimeric dialkylaluminiumazide forming a 12-membered heterocycle as mentioned before (113.9 pm on average) [14]. The Al–N distances are very long [18] (205.8 and 208.9 pm) and indicate some steric stress in the molecule in accordance with the unusual angles Al–N–N and Al–C–Al.

The Al–O distances (189.1 pm) in the acetato compound **8** are in an expected range and similar to those observed for few compounds known in literature with acetato groups bridging two aluminium atoms [19]. A quite similar compound was recently obtained in our group $[R_2Al(\mu\text{-}H)(\mu\text{-}OOCPh)AlR_2$; $R = CH(SiMe_3)_2]$, in which the CH_2 and acetato groups of **8** are replaced by a bridging hydride ion and a benzoato group [20]. In this compound, the Al–O bond lengths are shortened to 183.8 pm on average. The C–O bond lengths in **8** are 126.3 and 124.9 pm, which is in the characteristic range of carboxylato groups with a delocalized C–O π bond [19,20].

The sodium atoms in both compounds are coordinated by six oxygen atoms of the crown ether [18]crown-6 (Na–O = 246.4 to 266.4 pm in **7** and 252.7 to 265.3 pm in **8**) and one oxygen atom of an diisopropyl ether molecule (Na–O 255.4 and 254.6 pm, respectively) with a distorted coordination geometry.

4. Experimental

All procedures were carried out under purified argon in dried solvents (diethyl ether and diisopropyl ether over Na/benzophenone; cyclopentane over $LiAlH_4$). Compound **1** was synthesized as described in Ref. [2], commercially available crown ether [18]crown-6, sodium azide, and sodium acetate were thoroughly evacuated at elevated temperature and used without further purification.

4.1. Synthesis of $[(\mu\text{-}N_3)R_2AlCH_2AlR_2]^- \{[Na([18]crown\text{-}6)[O(iPr)_2]\}^+$

7: An excess of solid NaN_3 (0.054 g, 0.831 mmol) was treated with a solution of 0.398 g (0.565 mmol) of **1** and 0.167 g (0.633 mmol) of the crown ether [18]crown-6 in 40 ml of diethyl ether; the colorless mixture was stirred at r.t. for 24 h. The solution was concentrated in vacuo at r.t. and cooled to −25°C. A small quantity of a colorless precipitate formed, which was rejected. The mother liquor was evaporated in vacuo to dryness, and the residue was dissolved in 1.5 ml of diisopropyl ether. Colorless crystals of the product were obtained at −50°C, they became amorphous upon evacuation at r.t. and contained less than one molecule diisopropylether in each formula unit. Yield: 0.344 g (54%). M.p. (argon, sealed capillary): 162°C. ^1H-NMR ($[D_{10}]Et_2O$, 300 MHz): δ 3.69 (s, 24 H, [18]crown-6), 1.05 (d, Me of diisopropyl ether), 0.11 (s, 72 H, $SiMe_3$), −1.05 (s, 4 H, $AlCHSi_2$), −1.52 (s, 2 H, $AlCH_2Al$). ^{13}C-NMR ($[D_{10}]Et_2O$, 75.5 MHz): δ 69.8 (OCH_2 of crown ether), 68.6 (CH of diisopropyl ether), 23.2 (Me of diisopropyl ether), 5.8 ($SiMe_3$), 5.0 ($AlCSi_2$), 2.0 (br., $AlCH_2Al$). IR (CsBr, paraffin): $\tilde{\nu} = 2112$ m cm^{-1} νN_3; 1462 vs, 1377 m paraffin; 1354 m, 1296 w, 1242 s δCH_3; 1111 s νCC, νCO; 1013 m δCH; 951 w, 920 m, 909 m, 843 vs, 775 s, 748 s, 725 w $\rho CH_3(Si)$; 667 s $\nu_{as}SiC$; 631 w, 608 w $\nu_s SiC$; 561 w, 517 w, 509 w, 465 w, 448 vw νAlC, νAlN; 372 vw δSiC.

4.2. Synthesis of $[(\mu\text{-}O_2C\text{-}CH_3\text{-}O,O')R_2AlCH_2AlR_2]^-$-$\{[Na([18]crown\text{-}6)[O(iPr)_2]\}^+$

8: An excess of solid sodium acetate (0.106 g, 1.29 mmol) was treated with a solution of 0.473 g (0.6723 mmol) of **1** and 0.182 g (0.689 mmol) of the crown ether [18]crown-6 in 50 ml of diethyl ether. The colorless mixture was stirred at r.t. for 24 h. After filtration the solvent was distilled off in vacuo. The residue was treated with 2 ml of cyclopentane, and diisopropyl ether was added dropwise, until a clear solution was obtained. The product crystallized at −65°C. The colorless crystals became amorphous upon evacuation at room temperature. Yield: 0.507 g (65%). M.p. (argon, sealed capillary): 180°C. ^1H-NMR ($[D_{10}]Et_2O$, 300 MHz): δ 3.68 (s, 24 H, crown ether), 2.00 (s, 3 H, Me of acetate), 1.05 (d, diisopropyl ether), 0.09 and 0.07 (each: s, 36 H, $SiMe_3$), −1.16 (s, 4 H, $AlCHSi_2$), −1.45 (s, 2 H, $AlCH_2Al$). ^{13}C-NMR ($[D_{10}]Et_2O$, 75.5 MHz): δ 179.3 (CO of acetate), 69.8 (crown ether), 68.6 (CH of diisopropyl ether), 23.2 (Me of diisopropylether), 25.9 (Me of acetate), 6.1 and 5.9 ($SiMe_3$), 3.6 ($AlCSi_2$); $AlCH_2Al$ not observed. IR (CsBr, paraffin): $\tilde{\nu} = 1582$ vs cm^{-1} νCO_2; 1464 vs, 1377 vs paraffin; 1354 s, 1296 s, 1250 vs, 1238 vs δCH_3; 1167 m, 1111 vs νCC, νCO; 1011 vs δCH; 961 s, 922 vs, 895 vs, 845 vs, 775 vs, 748 vs, 723 v $\rho CH_3(Si)$; 667 vs, 662 vs $\nu_{as}SiC$; 627 m $\nu_s SiC$; 581 m, 550 vs, 519 m, 505 m, 463 w, 451 w, 409 w νAlC, νAlO; 374 w, 351 vw δSiC.

Table 1
Crystal data, data collection parameters and structure refinement for **7** and **8** [a]

	7	**8**
Formula	$C_{47}H_{116}N_3O_7NaAl_2Si_8$	$C_{55}H_{119}O_9NaAl_2Si_8$
Crystal system	Monoclinic	Triclinic
Space group [21]	$P2_1/c$; No. 14	$P\bar{1}$; No. 2
Z	4	2
Temperature (K)	213(2)	213(2)
$D_{calc.}$ (g cm^{-3})	1.064	1.055
a (pm)	1484.2(3)	1198.1(2)
b (pm)	1508.5(3)	1549.2(3)
c (pm)	3175.1(6)	2178.2(4)
α (°)	90	79.56(3)
β (°)	93.18(3)	76.25(3)
γ (°)	90	85.84(3)
V (10^{-30} m^3)	7098(2)	3860(1)
μ (mm^{-1})	0.223	0.210
Crystal size (mm)	$0.85 \times 0.38 \times 0.32$	$1.06 \times 0.81 \times 0.67$
Diffractometer	Stoe-IPDS	Stoe-IPDS
Radiation	Mo–K_α; graphite monochromator	
Scan mode (number of exposures; $\Delta\varphi$)	150, 1.2°	310, 1.0°
2Θ range (°)	$3.9 \leq 2\Theta \leq 52.1$	$4.3 \leq 2\Theta \leq 52.0$
Index ranges	$-18 \leq h \leq 18$	$-14 \leq h \leq 14$
	$0 \leq k \leq 18$	$-19 \leq k \leq 19$
	$0 \leq l \leq 36$	$-26 \leq l \leq 26$
Independent reflections	13309	14041
Reflections $F > 4\ \sigma(F)$	7160	9984
Parameters	641	900
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ ($F > 4\sigma(F)$)	0.047	0.074
$wR^2 = \{\Sigma w(\|F_o\|^2 - \|F_c\|^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$ (all data)	0.085	0.209
Max./min. residual electron density (10^{30} e m^{-3})	0.52/−0.46	0.87/−0.76

[a] Programmes SHELXL-93; SHELXTL [22]; solutions by direct methods, full matrix refinement with all independent structure factors.

4.3. Crystal structure determinations

Single crystals of compound **7** were obtained by recrystallization from diisopropyl ether. Compound **8** crystallized from a mixture of cyclopentane and diisopropyl ether. The crystals included solvent molecules and became rapidly amorphous after isolation. Therefore, they were directly taken from the solution and mounted on the diffractometer by using a perfluorinated polyether. Crystal data and structure refinement parameters are given in Table 1 [23]. The complex cation in compound **8** was disordered, and all atoms of the ether molecules occupied two positions, which could be refined completely with occupancy factors of 0.72 and 0.28. Further, the crystals included a severely disordered diisopropyl ether molecule, which by the superposition of atoms gave a six-membered ring. The disorder could not be resolved completely, and the atoms of the ring were refined as carbon atoms.

Acknowledgements

We are grateful to the Fonds der Chemischen Industrie for generous financial support.

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[23] The crystallographic data of **7** and **8** (excluding structure factors) were deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-104482 (**7**) and -104483 (**8**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, GB-Cambridge CB2 1EZ, UK (fax: +44-(1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk).